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Heavy metal pollution recorded in Porites corals from Daya Bay,

northern South China Sea

Tian-Ran Chen^{a*}, Ke-Fu Yu^{a,b}, Shu Li^a, Gilbert J. Price^b, Qi Shi^a, Gang-Jian Wei^c

Affiliations:

a Key Laboratory of Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese

Academy of Sciences, Guangzhou 510301, China

b Radiogenic Isotope Laboratory, Center for Microscopy and Microanalysis, The University of

Queensland, Qld 4072, Australia

c Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of

Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

*Corresponding author

Tel.: +86 20 89023341; fax: +86 20 84451672

E-mail address: chentianran2008@gmail.com (T. R. Chen).

ABSTRACT

We examined metal-to-calcium ratios (Fe/Ca, Mn/Ca and Zn/Ca) in the growth bands of two *Porites* corals from Daya Bay, South China Sea, in order to trace long-term trends in local ambient pollution levels. Although Fe and Mn did not show any obvious increasing trends over 32 years in the period 1976-2007, peak values of Fe/Ca and Mn/Ca occurred in the mid-late 1980s, temporally-coeval with the local construction of a nuclear power station. Furthermore, both corals showed rapid increases in Zn concentrations over the past 14 years (1994-2007), most likely due to increases in domestic and industrial sewage discharge. The Daya Bay corals had higher concentrations of metals than other reported corals from both pristine and seriously polluted locations, suggesting that acute (Fe and Mn) and chronic (Zn) heavy metal contamination has occurred locally over the past ~32 years.

Key-words: Heavy metals, Pollution monitoring, *Porites* corals, Coastal zone, Daya Bay, South China Sea

1. Introduction

As a marginal sea surrounded by land, the South China Sea (SCS) has been heavily impacted by human activities, especially its estuaries and bays which are seriously threatened by high rates of population growth as well as agricultural and industrial developments (Scott, 1990; Morton, 2001). Daya Bay, located in the subtropical region of the northern SCS (Fig. 1), is one of the most important economic development districts and aquaculture areas in China. The first commercial nuclear power station in Mainland China, the Daya Bay Nuclear Power Station (DNPS), is located here. Since the 1980s, however, rapid expansions of urbanization, aquaculture, and industry have adversely affected the water quality in Daya Bay. There is mounting evidence for notable environmental deterioration in Daya Bay, such as degradation in water quality (e.g. nutrients, pH, COD, BOD, DO, Chl a) (Wang et al., 2006, 2008a; Wu and Wang, 2007; Wu et al., 2009), increased organic contaminants (e.g. DDT, PAH, PCB) in water and sediments (Zhou et al., 2001; Zhou and Maskaoui, 2003; Wang et al., 2008b; Xing et al., 2009; Yan et al., 2009), thermal pollution from the DNPS (Tang et al., 2003), and episodes of harmful algal blooms (Song et al., 2004, 2009; Yu et al., 2007a, 2007b). Large coastal constructions, such as the DNPS and Huizhou Port, have caused a significant increase in sedimentation input into seawater, however, the impacts on water quality and ecosystems are still unclear. Plastics manufacturing, petrochemical, printing and other industries are continually emerging around Daya Bay and surrounding areas (Song et al., 2009). As such, monitoring of long-term heavy metal pollution is crucial to the management of this area. Moreover, heavy metals can remain unchanged in the environment for years and may thus pose a threat to marine organisms and humans. For example, accumulation of heavy metals in aquacultural seafood is potentially harmful to human health. However, monitoring is still

non-existent in the bay. Du et al. (2008) profiled 100 years of heavy metal history in the sediments via 4 cores (dated by ²¹⁰Pb) drilled in Dapeng'ao cove (Fig. 1), Daya Bay, and the results showed that the concentrations of As (7.7-30.8 mg/kg), Cd (23.2-60.5 μg/kg), Cr (22.1-48.1 mg/kg), Pb (22.0-111.0 mg/kg), Cu (4.9-24.1 mg/kg) and Zn (57.5-120.0 mg/kg) increased gradually from the bottom (i.e., oldest) to the surface (i.e., youngest) layer for all core samples. However, heavy metal trends in Daya Bay sediments may not clearly represent their variations in aquatic systems, because slow sedimentation rates and biological effects tend to obscure short-term variations in metal levels.

Scleractinian corals, such as *Porites*, have proved to be excellent material for high-resolution paleoclimatic (or other historical events) reconstruction as they are widely distributed, sensitive to environmental changes, and their annual growth bands can be accurately dated (Gagan et al., 2000; Yu et al., 2005). Furthermore, they have a high tendency to accumulate metals continuously in their skeletons during growth and have therefore been suggested to be useful indicators of historical pollution events such as chronic (long-term) metal pollution, including oceanic lead contamination linked with gasoline and other industries (Dodge and Gilbert, 1984; Shen and Boyle, 1987; Medina-Elizalde et al., 2002; Inoue et al., 2006; Inoue and Tanimizu, 2008; Kelly et al., 2009), and sewage and industrial discharges (Hanna and Muir, 1990; Scott, 1990; Guzmán and Jiménez, 1992; Runnalls and Coleman, 2003; Ramos et al., 2004; Al-Rousan et al., 2007). They may also record relatively short-time (few months or years) acute metal pollution caused by some specific events such as mining (David, 2000, 2003; Fallon et al., 2002; Edinger et al., 2008) and harbor dredging (Esslemont, 2000; Esslemont et al., 2004). However, little attention has been focused on metal pollution caused by large-scale coastal construction.

Metal elements are incorporated into corals by a variety of pathways, such as direct replacement of calcium by dissolved metals in aragonite lattice, inclusion of detritus materials into skeletal pore spaces, uptake of organic materials incorporation of metals into coral skeletons, or coral feeding (see review by Howard and Brown, 1984; Hanna and Muir, 1990). It has been well documented (Hanna and Muir, 1990; Esslemont, 2000; Ramos, et al. 2004) that corals from polluted areas show a much higher concentration of trace metals in their skeletons than corals from unpolluted areas. The history of marine pollution is not well known in regions such as Daya Bay due to the lack of continuous monitoring systems. However, bio-monitoring techniques based on elemental concentrations in annual coral skeletons can be used to overcome this problem.

Non-reefal coral communities are patchily and sporadically distributed along offshore islands in Daya Bay (Chen et al., 2009). The aims of this study are to: (1) establish baseline levels of trace metals (Fe, Mn, Zn) in corals from a typical bay effected by various human activities in the northern SCS; (2) investigate temporal variation of metals in the aquatic environment by examining long-term (32 years) heavy metal variations in the growth bands of local *Porites* corals; and (3) investigate the role of corals as biomonitors of metal pollution in the water environment of Daya Bay.

2. Materials and methods

2.1. Coral Collection

Two coral specimens of living *Porites* were collected for metal analysis. One (DLJ-1) was collected in June, 2006, from a depth of approximately 1 m on the rocky substratum off Dalajia Island (Fig. 1). The other specimen (XLJ-1) was collected in August, 2007, from a depth of

approximately 3 m off Xiaolajia Island (Fig. 1). Both of these islands are uninhabited with low topographic relief and large rocks.

2.2. Sub-sampling procedure

The coral samples were washed with freshwater then sectioned by a water-lubricated diamond-bit masonry saw to obtain a parallel slab, approximately 8 mm in thickness, containing the axis of maximum growth of the coral. Dry coral slabs were X-radiographed to expose density banding (Fig. 2). The coral slabs were soaked in 10% H₂O₂ for 48 h, cleaned for 20 min in an ultrasonic bath containing Milli-Q water (3 times), and then oven dried at 60 °C for 48 h.

Using the X-radiographs as guides, skeletal sub-samples were manually scraped with a thin blade along the slab. From the surface downward, a total of 410 and 495 sub-samples were taken from DLJ-1 and XLJ-1, respectively. For XLJ-1, 191 sub-samples were selected for additional metal analysis, based on Sr/Ca and Mg/Ca chronologies. Thus, total of 601 sub-samples were analyzed for heavy metals. For each sub-sample, about 50-60 mg of powdered sample was placed in a 15 ml centrifuge tube and weighed, dissolved in 3% HNO₃. The resulting solution was then diluted to 2000 times. Before analysis, the mixture was centrifuged at 4000 r/min for 7 min.

In the analysis, all chemical pre-treatments were conducted in a super-purified laboratory in the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Only acid-cleaned bottles and centrifuge tubes were used and ultra high purity grade nitric acid was prepared by sub-boiling distillation. 3% HNO₃ (diluted with Milli-Q water) was prepared for blanks, dilution of standard solutions and sub-sample digestion.

2.3. Analytical methods

Sr/Ca and Mg/Ca values in coral skeletons vary with the ambient sea surface temperature (SST) and display seasonal cycles (Beck et al., 1992; Mitsuguchi et al., 1996). Using this relationship, we confirmed growth chronologies and time series of metal concentrations by measuring Sr/Ca and Mg/Ca values. The profiles of Sr/Ca and Mg/Ca both showed marked seasonal cycle characters (Fig. 2) and indicated an approximately linear response to SST, especially during cold winters, with sharp/narrow winter peaks observed corresponding to low SST values.

Trace metal (Fe, Mn and Zn) analyses were performed using an inductively coupled plasma atomic emission spectroscopy (ICP-AES), equipped with CCD photomultiplier tubes for simultaneous collection of all spectral lines within the analytical wave range (Varian Vista-Pro CCD Simultaneous ICP-AES). Procedural blank and calibration standards were reanalyzed every 20 samples and a quality control standard was reanalyzed every 5 samples for monitoring and correcting instrumental drift. Calibration standards were made with high Ca concentrations to match the chemical matrix of the samples. The relative standard deviation (RSD) of Fe, Mn and Zn measurements were 1.6%, 1.2% and 3.5%, respectively, based on analysis of 10 replicates of the Chinese national carbonate standard (GBW07129). Analytical methods for Ca, Mg and Sr were similar to those for Fe, Mn and Zn, except that the sub-sample solution was accurately diluted to 10000 times, because of the extremely strong intensity of their spectral lines.

3. Results

Time series of coral metal concentrations were constructed using seasonal cycles of Sr/Ca

and Mg/Ca. The skeletons of *Porites* corals DLJ-1 and XLJ-1 encompassed 25 (1982-2006) and 32 (1976-2007) years, respectively. These time scales conveniently spanned the period immediately before and after the period of rapid industrial development in Daya Bay (1980s). Significantly, our high-resolution sub-sampling approach provided overall monthly resolution for coral DLJ-1, and two-monthly resolution for coral XLJ-1. Figures 3 and 5 depict the analytical results for the mole ratios of Fe/Ca, Mn/Ca and Zn/Ca within each dated sub-sample from both coral specimens.

The metal element profiles for Fe and Mn from the two corals displayed similar patterns, especially the synchronous peaks in the 1985 layers for each coral (Fig. 3). Peaks of Fe/Ca and Mn/Ca occurred between the 1984 to 1989 layers in the DLJ-1 coral skeleton, followed by a dramatic decrease to low levels for subsequent years. An additional peak for Fe/Ca occurred in the 1994 layer. The average values for Fe/Ca and Mn/Ca were 120.01 and 2.88 µmol/mol, respectively. Peaks of Fe/Ca and Mn/Ca in XLJ-1 were narrow and low compared with those in DLJ-1. Both values were low before 1984, increased from 1984 to 1988, with the Fe/Ca ratios exhibiting remarkable fluctuation after 1990. In spite of relatively low values after 1990, Fe/Ca and Mn/Ca ratios were still higher than those obtained before 1984. A second Mn peak was observed at the outermost layer of the coral. The average values of Fe/Ca and Mn/Ca in coral XLJ-1 were 142.46 and 3.27 µmol/mol, respectively. The values of metals/Ca in both corals are similar (Fig. 3), except for Zn (Fig. 5).

The concentration of zinc in DLJ-1 was consistently greater than that in XLJ-1. However, both time series exhibited increasing zinc concentrations since 1994 (Fig. 5). The mean values of Zn/Ca in DLJ-1 and XLJ-1 were 17.72 and 5.58 µmol/mol, respectively. The highest

concentrations of Zn/Ca were recorded in the outmost (i.e., youngest) layers in both corals, and these were much higher than the values before 1994.

4. Discussion

4.1. Fe/Ca and Mn/Ca variations and their response to the construction of the nuclear power stations

Mn/Ca followed a similar pattern to Fe/Ca (Fig. 3), and the correlation between the ratios of Fe/Ca and Mn/Ca in the two corals was significant (DLJ-1, r=0.67, p<0.001, n= 410; XLJ-1, r=0.56, p<0.001, n=191) suggesting common sources for both. It is likely that they are also regulated by the same geochemical processes in seawater, with the mechanisms of uptake of these two elements into the calcareous matrix also being similar (Hanna and Muir, 1990). For example, Fe and Mn have been hypothesized to substitute for calcium in the aragonite lattice (Fallon et al., 2002; David, 2003).

Fe and Mn are regarded as markers of terrestrial material inputs (Ramos et al., 2004; Ramos et al., 2009). For example, Lewis et al. (2007) described Mn in a 175 yr-long *Porites* coral from Magnetic Island, Australia, as a tracer of sediment input attributed to animal grazing and related soil erosion, from the Burdekin River catchment into the Great Barrier Reef lagoon. Fallon et al. (2002) and David (2003) observed trends in Mn in *Porites* corals from Papua New Guinea and the Philippines respectively, and hypothesized that its long-term variation was due to sediment input as a result of local mining activities. However, Daya Bay is a semi-enclosed bay with minor seasonal streams, rather than major rivers, draining into it (Xu, 1989). Therefore, it is unlikely that Fe and Mn in *Porites* corals in Daya Bay are derived from significant coastal runoff and river

input.

Two nuclear power stations, Daya Bay Nuclear Power Station (DNPS) and Ling'ao Nuclear Power Station (LNPS), situated on the north shore of Dapeng'ao Cove (Fig. 1), began power operations in 1994 and 2002, respectively. Interestingly, Fe/Ca and Mn/Ca ratios in the *Porites* corals showed dramatic increases at the beginning of 1984, and then dropped to low levels in late 1989 (Fig. 3), corresponding with the timing of the DNPS construction (Table 1).

When DNPS construction began, major projects such as deforestation, blasting, flattening of the hilltops and land leveling (Fig. 4) caused a significant increase in sedimentation via the exposure of soils to the erosive forces of heavy rain runoff and wind. The rainy season in Daya Bay is between April and September, with typhoons commonly occurring during the summer (Xu, 1989) leading to increased sedimentary input into the bay. Additionally, waste soil dumping and land-filling caused bulk amounts of soil to be dumped directly into the bay during the constructions (Fig. 4). As such, it is highly likely that sediments (soils) containing high values of Fe and Mn caused the Fe/Ca and Mn/Ca peaks recorded in the *Porites* coral skeletons from Dalajia and Xiaolajia Islands (both islands are adjacent to the construction site; Fig. 1). Relatively low levels of Fe and Mn in 1986 correspond well with the end of the land leveling projects, with the later peaks having occurred during subsequent activities such as digging (foundations) and building construction (Table 1, Fig. 3).

Pre-construction levels (pre-1984) for the Fe and Mn were low in both corals: 118.87 μmol/mol (Fe/Ca, 1976-1983) and 2.68 μmol/mol (Mn/Ca, 1976-1983) for XLJ-1, and 76.08 μmol/mol (Fe/Ca, 1982-1983) and 1.50 μmol/mol (Mn/Ca, 1982-1983) for DLJ-1. However, the coral metals increased dramatically after DNPS construction began in 1984. The maximum values

of Fe/Ca and Mn/Ca in the XLJ-1 skeleton were 411.24 and 9.83 μmol/mol, indicating an approximate 3.5-fold increase since the pre-construction levels, indicating severe acute pollution. After 1990, the concentrations of Fe and Mn returned to relatively low levels, but the ratios of Fe/Ca and Mn/Ca were still higher than pre-construction levels (XLJ-1, Fe/Ca 140.37 μmol/mol, Mn/Ca 3.20 μmol/mol, 1990-2007; DLJ-1, Fe/Ca 101.72 μmol/mol, Mn/Ca 2.07 μmol/mol, 1990-2006). The profiles of the Fe/Ca ratio fluctuated after 1994 in both corals (Fig. 3), possibly due to other pollution sources, for example, increased sewage discharges or harbor dredging.

The LNPS construction (Table 1) had little impact on the heavy metal concentrations in seawater according to the Fe/Ca and Mn/Ca profiles in corals, as the foundation work (e.g. land leveling, land-filling) had been completed during the DNSP construction (the power stations are adjacent, Fig. 1), and also probably because of more strict management during the works. For example, waste soils from excavations were carried away rather than being dumped directly into the bay.

4.2. Zn/Ca variations and its response to the recent increase in sewage discharge

Zn/Ca showed a distinctive profile in both *Porites* corals, exhibiting a gradually increasing content since 1994 (Fig. 5). The ratios of Zn/Ca in DLJ-1 and XLJ-1 gradually increased to 49.02 μmol/mol in 2006 and 34.20 μmol/mol in 2007, respectively, corresponding to 5-fold and 16-fold increases relative to the baseline values before 1994 (10.26 μmol/mol for DLJ-1, and 2.06 μmol/mol for XLJ-1).

Increased Zn levels in contemporary scleractinian coral skeletons commonly have strong anthropogenic sources (Hanna and Muir, 1990; Guzmán and Jiménez, 1992; Esslemont, 2000;

Runnalls and Coleman, 2003; Ramos et al., 2004; Al-Rousan et al., 2007). At Daya Bay, Zn/Ca levels in the corals exhibit a progressively increasing trend since 1994, corresponding to the commencement of operation of the DNPS. During the summer and autumn months, the thermal plumes of DNPS alone may extend as far as 8-10 km south along the coast (Tang et al., 2003), and this does not include the LNPS operation which started after 2002. Therefore, thermal effluents from the two nuclear power stations may extend as far as Xiaolajia and Dalajia Islands. Heavy metals (probably leached from condensers, antifouling or antirust treatments, etc.) in thermal plumes may be recorded in corals along the two islands. If this were the case, however, the Zn/Ca profiles would display two peaks (corresponding to commencement of operations DNPS and LNPS respectively) in the form of steps rather than a gradual increase. Each station has only two power units that have been present since operations started, and new units have not been added since.

In a different study, Huang et al. (1991) examined the water quality (except for seawater temperature) along the shallow part near the cooling water outlet of the Third Nuclear Power Plant, Southern Taiwan. On the basis of low concentrations of mercury, chromium, zinc, cadmium, lead and copper, Huang et al. (1991) suggested that the water quality was not impacted by thermal discharge. It is also possible that the thermal effluents from DNPS and LNPS had little influence on the metal concentrations in near shore seawater at Daya Bay.

Other possible sources of zinc in corals from Daya Bay include domestic and industrial sewage discharge, and input from other point sources such as oil terminals and ports. High rates of population growth and industrial development have occurred in Daya Bay during the last 30 years (Wang et al., 2008a), with major increases since 1994 (Fig. 6). Locally, industrial sewage (which

typically contains heavy metal contamination) is mainly discharged from the industrial area distributed along the north coast of Daya Bay. Contaminants are most likely transported and distributed by currents (north-south currents during rising- and ebb- tides) through the entire region (Fig. 7). The Zn/Ca patterns in corals revealed that the Zn content in seawater has been increasing since 1994, coeval with the timing of rapid growth of population and industry. The aquatic environment of Daya Bay has been progressively impacted by Zn contamination since that time. Our interpretation is consistent with other studies throughout the world where it has been observed that high levels of Zn in seawater are derived mostly from industrial discharges (Hanna and Muir, 1990; Guzmán and Jiménez, 1992; Esslemont, 2000; Runnalls and Coleman, 2003; Ramos et al., 2004; Al-Rousan et al., 2007).

The gradually increasing Zn levels in corals indicate chronic pollution in the Daya Bay seawater after 1994. Although zinc is an important metal at trace concentrations, it may also be very toxic when in excess, as demonstrated in trace metal toxicological studies on zooxanthellae (Goh and Chou, 1997) and fertilization (Reichelt-Brushett and Harrison, 2005) of corals. The potential harmful effect of Zn pollution on corals and other fauna within Daya Bay requires significant ongoing monitoring.

4.3. Comparison with previous studies

There is little doubt that the Daya Bay *Porites* corals have been highly contaminated as a result of significant local anthropogenic impacts. In fact, at Daya Bay, the elements Fe, Mn and Zn are present in quantities as great, if not greater, than highly contaminated corals from other regions throughout the world (Table 2).

Fe concentrations in the corals collected from Daya Bay were higher than the range observed in corals from other seriously polluted regions, such as the Red Sea (Hanna and Muir, 1990; Al-Rousan et al., 2007) and India (Jayaraju et al., 2009), and approached the highest coral Fe values reported by Bastidas and García (1999) of 369.31 µg/g for Venezuela. The highest coral Mn values for Daya Bay (mid-late 1980's) are also similar to values recorded for highly-polluted areas of the Red Sea (Hanna and Muir, 1990; Al-Rousan et al., 2007). However, Fe and Mn levels in Daya Bay corals decreased after 1989, indicating that the region suffered acute pollution during the coastal construction of DNPS in the mid-1980s.

Zn concentrations in corals from other polluted and pristine areas typically range from 0.68 μg/g (Fallon et al, 2002) to 118.03 μg/g (Lee and Mohamed, 2009) (Table 2). Although corals from Daya Bay had peak values close to the lower end of the range (22.28 and 31.59 μg/g), the concentrations are much higher than corals from pristine areas such as some isolated islands of Japan (Ramos et al., 2004), and even seriously polluted areas such as the Philippines (David, 2003) and Gulf of Aqaba, Jordan (Al-Rousan et al., 2007). Our data suggests that Zn pollution in the seawater environment of Daya Bay has gradually increased to relatively high levels, with the highest concentrations being recorded in the most recent growth periods of the corals (Fig. 5). A similar trend of gradually increasing Zn was found in a *Porites* coral from Dafangji Island (21°21′ N, 111°11′ E), Guangdong Province, China, where the Zn levels increased from 4.2 to 55.1 μg g⁻¹ over 20 years (1982-2001) as a result of industrial discharges from the coastal area (Peng et al., 2006). Studies of metal concentrations in corals from Hong Kong (Scott, 1990), Dafangji Island (Peng et al., 2006) and Daya Bay (this study) each show evidence that the coastal areas in the northern SCS have been highly contaminated by heavy metals.

5. Conclusions

In this paper, we explored the long-term environmental impacts of a large project (DNPS construction) along the western coast of Daya Bay, South China Sea. We examined heavy metal variations (Fe, Mn and Zn) in ~32 year long growth bands of *Porites* corals as a proxy of historic pollution in the region.

Fe and Mn concentrations in the Porites coral skeletons collected from Dalajia and Xiaolajia Island did not show an obvious increasing trend over the past 32 years. However, significantly higher Fe and Mn concentrations were observed in the 1984-1989 growth bands of the corals- a time period that coincided with the construction of the Daya Bay Nuclear Power Station. Increased sediment input as a direct result of human alteration of the landscape (e.g. deforestation, blasting, land leveling, land-filling, and dumping) for the DNPS construction was likely the primary source of elevated levels of Fe and Mn in the corals. The concentration of Zn in the Daya Bay corals increased dramatically relative to the baseline value since 1994, corresponding well to the period of rapid local population and industrial development. The elevated levels, which have gradually increased through to the present, were most likely caused by contributions from domestic and industrial sewage discharge into the bay. Comparisons with other studies on heavy metal concentrations in coral skeletons from different regions suggests that Daya Bay has suffered from serious heavy metal pollution and is exhibiting a trend of continuous deterioration. Further and ongoing monitoring of the Zn concentration in Daya Bay is critical. Our present study suggests that heavy metals must be considered a serious regional threat in Daya Bay, and other marginal regions in the South China Sea.

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References

- 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.
- 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(10), 899-907.
- Beck, J.W., Edwards, R.L., Ito E., Taylor, F.W., Recy, J., Rougerie, F., Joannot, P., Henin, C., 1992. Sea-surface temperature from coral skeletal strontium/calcium ratios. Science 257, 644-647.
- Chen, T.R., Yu, K.F., Shi, Q., Li, S., Price, G.J., Wang, R., Zhao, M.X., Chen, T.G., Zhao, J.X., 2009. Twenty-five years of change in scleractinian coral communities of Daya Bay (northern South China Sea) and its response to the 2008 AD extreme cold climate event. Chinese Science Bulletin 54(12), 2107-2117.
- David, C.P., 2000. Tracing a mine tailings spill using heavy metal concentrations in coral growth bands:

 Preliminary results and interpretation. Proceedings of the 9th International Coral Reef Symposium 2,

 23-27.

- David, C.P., 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.
- Dodge, R.E., Gilbert, T.R., 1984. Chronology of lead pollution contained in banded coral skeletons. Marine Biology 82, 9-13.
- Du, J.Z., Mu, H.D., Song, H.Q., Yan, S.P., Gu, Y.J., Zhang, J., 2008. 100 years of sediment history of heavy metals in Daya Bay, China. Water, Air, & Soil Pollution 190, 343-351.
- Edinger, E.N., Azmy, K., Diegor, W., Siregar, P.R., 2008. Heavy metal contamination form gold mining recorded in *Porites labata* skeletons, Buyat-Ratototok district, North Sulawesi, Indonesia. Marine Pollution Bulletin 56, 1553-1569.
- Esslemont, G., 2000. Heavy metals in seawater, marine sediments and corals from the Townsville section, Great Barrier Reef Marine Park, Queensland. Marine Chemistry 71, 215-231.
- Esslemont, G, Russell, R.A., Maher, W.A., 2004. Coral record of harbour dredging: Townsville, Australia. Journal of Marine Systems 52, 51-64.
- 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(1), 45-62.
- Gagan, M.K., Ayliffe, L.K., Beck, J.W., Cole, J.E., Druffel, E.R.M., Dunbar, R.B., Schrag, D.P., 2000. New views of tropical paloclimates from corals. Quaternary Science Reviews 19, 45-64.
- Goh, B.P.L., Chou, L.M., 1997. Effects of the heavy metals copper and zinc on zooxanthellae cells in culture.

 Environmental Monitoring and Assessment 44, 11-19.
- Guzmán, H.M., Jiménez, C.E., 1992. Contamination of coral reefs by heavy metals along the Caribbean coast of central America (Costa Rica and Panama). Marine Pollution Bulletin 24(11), 554-561.
- Hanna, R.G., Muir, G.L., 1990. Red sea corals as biomonitors of trace metal pollution. Environmental Monitoring

- and Assessment 14, 211-222.
- Howard, L.S., Brown, B.E., 1984. Heavy metals and reef corals. Oceanography and Marine Biology: An Annual Review 22, 195-210.
- Inoue, M., Hata, A., Suzuki, A., Nohara, M., Shikazono, N., Yim, W.W.S., Hantoro, W.S., Sun, D.H., Kawahata, H., 2006. Distribution and temporal changes of lead in the surface seawater in the western Pacific and adjacent seas derived from coral skeletons. Environmental Pollution 144, 1045-1052.
- Inoue, M., Tanimizu, M., 2008. Anthropogenic lead inputs to the western Pacific during the 20th century. Science of the Total Environment 406, 123-130.
- Jayaraju, N., Sundara Raja Reddy, B.C., Reddy, K.R., 2009. Heavy metal pollution in reef corals of Tuticorin Coast, Southeast Coast of India. Soil and Sediment Contamination 18, 445-454.
- 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.
- Lee, J.N., Mohamed, C.A.R., 2009. Trace metal contents in the Porites corals of Peninsular Malaysia. International Journal of Environmental Research 3(1), 85-94.
- 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.
- Medina-Elizalde, M., Gold-Bouchot, G., Ceja-Moreno, V., 2002. Lead contamination in the Mexican Caribbean recorded by the coral *Montastraea annularis* (Ellis and Solander). Marine Pollution Bulletin 44, 421-431.
- Mitsuguchi, T., Matsumoto, E., Abe, O., Uchida, T., Isdale, P.J., 1996. Mg/Ca thermometry in coral skeletons. Science 274, 961-963.

- Morton, B., Blackmore, G., 2001. South China Sea. Marine Pollution Bulletin 42, 1236-1263.
- Peng, Z.C., Liu, J.H., Zhou, C.L., Nie, B.F., Chen, T.G., 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(2), 132-138.
- Ramos, A.A., Inoue, Y., Ohde, S., 2004. Metal contents in *Porites* corals: anthropogenic input of river run-off into a coral reef from an urbanized area, Okinawa. Marine Pollution Bulletin 48, 281-294.
- Ramos, R., Cipriani, R., Guzman, H.M., García, E., 2009. Chronology of mercury enrichment factors in reef corals from western Venezuela. Marine Pollution Bulletin 58, 222-229.
- Reichelt-Brushett, A.J., Harrison, P.L., 2005. The effect of selected trace metals on the fertilization success of several scleractinian coral species. Coral Reefs 24, 524-534.
- Runnalls, L.A., Coleman, M.L., 2003. Record of natural and anthropogenic changes in reef environments (Barbados West Indies) using laser ablation ICP-MS and sclerochronology on coral cores. Coral Reefs 22, 416-426.
- Scott, P.J.B., 1990. Chronic pollution recorded in coral skeletons in Hong Kong. Journal of Experimental Marine Biology and Ecology 139, 51-64.
- Shen, GT., Boyle, E.A., 1987. Lead in corals: reconstruction of historical industrial fluxes to the surface ocean.

 Earth and Planetary Science Letters 82, 289-304.
- Song, X.Y., Huang, L.M, Zhang, J.L, Huang, X.P., Zhang, J.B., Yin, J.Q., Tan, Y.H., Liu, S., 2004. Variation of phytoplankton biomass and primary production in Daya Bay during spring and summer. Marine Pollution Bulletin 49, 1036-1044.
- Song, X.Y., Huang, L.M., Zhang, J.L., Huang, H.H., Li, T., Su, Q., 2009. Harmful algal blooms (HABs) in Daya Bay, China: An in situ study of primary production and environmental impacts. Marine Pollution

- Bulletin 58, 1310-1318.
- Tang, D.L., Kester, D.R., Wang, Z.D., Lian, J.S., Kawamura H., 2003. AVHRR satellite remote sensing and shipboard measurements of the thermal plume from the Daya Bay, nuclear power station, China. Remote Sensing of Environment 84, 506-515.
- Wang, Y.S., Lou, Z.P., Sun, C.C., Wu, M.L., Han, S.H., 2006. Multivariate statistical analysis of water quality and phytoplankton characteristics in Daya Bay, China, from 1999 to 2002. Oceanologia 48(2), 193-211.
- Wang, Y.S., Lou, Z.P., Sun, C.C., Sun, S., 2008a. Ecological environment changes in Daya Bay, China, from 1982 to 2004. Marine Pollution Bulletin 56, 1871-1879.
- Wang, Z.Y., Yan, W., Chi, J.S., Zhang, G., 2008b. Spatial and vertical distribution of organochlorine pesticides in sediments from Daya Bay, South China. Marine Pollution Bulletin 56, 1578-1585.
- Wu, M.L., Wang, Y.S., 2007. Using chemometrics to evaluate anthropogenic effects in Daya Bay, China. Estuarine, Coastal and Shelf Science 72(4), 732-742.
- Wu, M.L., Wang, Y.S., Sun, C.C., Wang, H., Dong, J.D., Han, S.H., 2009. Identification of anthropogenic effects and seasonality on water quality in Daya Bay, South China Sea. Journal of Environmental Management 90, 3082-3090.
- Wu, R.H., Cai, S.Q., Wang, S.A., Zhang, W.J., 2007. Three-dimensional numerical simulation of tidal current and residual current at Daya Bay. Journal of Tropical Oceanography (in Chinese) 26(3), 18-23.
- Xing, Y.N., Guo, Y., Xie, M., Shen, R.L., Zeng, E.Y., 2009. Detection of DDT and its metabolites in two estuaries of South China using a SPME-based device: First report of *p,p*'-DDMU in water column. Environmental Pollution 157, 1382-1387.
- Xu, G.Z., 1989. Environments and resources of Daya Bay. Anhui Science and Technology Publishing House, Hefei, China.

- Yan, W., Chi, J.S., Wang, Z.Y., Huang, W.X., Zhang, G., 2009. Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from Daya Bay, South China. Environmental Pollution 157, 1823-1830.
- Yu, J., Tang, D.L., Oh, I.S., Yao, L.J., 2007a. Response of harmful algal blooms to environmental changes in Daya Bay, China. Terrestrial Atmospheric and Oceanic Sciences 18(5), 1011-1027.
- Yu, J., Tang, D.L., Wang, S.F., Lian, J.S., Wang, Y.S., 2007b. Changes of water temperature and harmful algal bloom in the Daya Bay in the Northern South China Sea. Marine Science Bulletin 9(2), 25-33.
- Yu, K.F., Zhao, J.X., Wei, G.J., Cheng, X.R., Wang, P.X., 2005. Mid-late Holocene monsoon climate retrieved from seasonal Sr/Ca and δ^{18} O records of *Porites lutea* corals at Leizhou Peninsula, northern coast of South China Sea. Global and Planetary Change 47, 301-316.
- Zhou, J.L., Maskaoui, K., Qiu, Y.M., Hong, H.S., Wang, Z.D., 2001. Polychlorinated biphenyl congeners and organochlorine insecticides in the water column and sediments of Daya Bay, China. Environmental Pollution 113, 373-384.
- Zhou, J.L., Maskaoui, K., 2003. Distribution of polycyclic aromatic hydrocarbons in water and surface sediments from Daya Bay, China. Environmental Pollution 121, 269-281.

Figure captions

- **Fig. 1.** Map of Daya Bay, South China Sea, indicating the sampling sites (Dalajia and Xiaolajia Island) and position of local nuclear power stations.
- Fig. 2. Sr/Ca, Mg/Ca ratios and X-radiography positive prints for *Porites* corals from Daya Bay.

 Annual banding within the skeleton is indicated by the cycles of high (dark) and low (light) density. Sub-sampling transects are indicated by white lines. Contrary to Mg/Ca ratios, Sr/Ca ratios are inversely correlated with SST so that the maximum of the sine-like record corresponds to the lowest winter temperature. The corresponding monthly SST was recorded at adjacent Zhelang Ocean Observation (22°39'N, 115°34'E).
- Fig. 3. Time series of Fe/Ca and Mn/Ca ratios in the Porites corals collected from Daya Bay
- **Fig. 4.** Pre-1984 topography at the site of the DNPS (upper) and post-1984 land leveling during its construction (below). Photos are from CGNPC, http://www.cgnpc.com.cn.
- Fig. 5. Time series of Zn/Ca ratios in the Porites corals collected from Daya Bay
- **Fig. 6.** Total industrial output values (**A**) and population changes (**B**) along the Daya Bay coast over last decades. Data are from Wang et al. (2008a).
- Fig. 7. Regional sea current patterns in Daya Bay (modified from Wu et al, 2007).

Table captions

- Table 1 Construction sequence of events of DNPS & LNPS in Daya Bay
- **Table 2** Heavy metal concentrations from comparative worldwide studies of *Porites*

Table 1

Construction sequence of events of DNPS & LNPS in Daya Bay

| Date | Construction processes | | | |
|----------------|---|--|--|--|
| April, 1984 | Deforestation, land leveling and land-filling | | | |
| March, 1986 | Digging and building construction (DNPS) | | | |
| December, 1989 | Construction ends (DNPS) | | | |
| 1990~1994 | Equipment installation and debugging (DNPS) | | | |
| February, 1994 | DNPS operation | | | |
| June, 1996 | Digging and building construction (LNPS) | | | |
| May, 1999 | Equipment installation and debugging (LNPS) | | | |
| May, 2002 | LNPS operation | | | |

Information from the website of China Guangdong Nuclear Power Holding Co., Ltd. (CGNPC), the governor of

DNPS and LNPS, http://www.cgnpc.com.cn

Table 2
Heavy metal concentrations from comparative worldwide studies of *Porites*

| Reference | Species | Location | Fe | Fe/Ca | Mn | Mn/Ca | Zn | Zn/Ca |
|---|--------------------|---------------------------------------|----------------------|-----------------------|---------------------|-----------------|---------------------|----------------------|
| | | | $(\mu g/g)$ | (µmol/mol) | $(\mu g/g)$ | $(\mu mol/mol)$ | $(\mu g/g)$ | $(\mu mol/mol)$ |
| Hanna, R.G., 1990 | Porites lutea | Jeddah, Saudi Arabia | 38±4 | 65 | 6.67±0.21 | 11 | 9.28±2 | 15.9 |
| Bastidas, C., 1999 Porites astreoides Porites astreoides | Porites astreoides | Punta Brava, Venezuela | 1.32-369.31 | | _ | - | 3.59-42.45 | |
| | | | (62.05) ^a | | | | $(10.67)^{a}$ | _ |
| | D 14 4 1 | Bajo Caimán, Venezuela | nd-88.68 | | - | _ | 0.83-23.10 | |
| | Porties astreolaes | | $(18.09)^{a}$ | | | | $(9.12)^{a}$ | _ |
| Fallon, S.J., 2002 | Porites sp. | Misima Island, Papua New Guinea | - , Ċ | _ | 0.19-1.6 | _ | 0.68-36.5 | _ |
| David, C.P., 2003 | Porites lobata | Ihatub reef, Philippines | - ^ | - | $(0.8)^{a}$ | _ | $(2.0)^{a}$ | _ |
| | Porites lobata | Ulan reef, Philippines | | _ | $(1.0)^{a}$ | _ | $(1.8)^{a}$ | _ |
| | Porites lobata | Caganhao reef, Philippines | - | _ | $(0.8)^{a}$ | _ | $(1.0)^{a}$ | _ |
| , , | Porites sp. | Hija River estuary, Japan | | | - | 0.172-7.58 | | 2.21-34.3 |
| | | | _ | _ | | $(2.13)^{a}$ | _ | (11.19) ^a |
| | Porites sp. | Rukan-sho, Japan | - | _ | _ | 0.173 | _ | 0.264 |
| Peng, Z.C., 2006 | Porites lutea | Dafangji Island, China | | | 2.76-6.85 | | 4.20-55.1 | |
| | | | _ | _ | (4.27) ^a | _ | (16.9) ^a | _ |
| Al-Rousan, S.A., 2007 | Porites sp. | Gulf of Aqaba, Jordan | 25.76±15.53 | _ | 8.22 ± 0.26 | _ | 5.52 ± 1.74 | _ |
| Lee, J.N., 2009 | Porites sp. | Pulau Tioman, Malasia | _ | _ | _ | _ | 23.73 | _ |
| | Porites sp. | Pulau Redang, Malasia | _ | _ | _ | | 39.96 | _ |
| | Porites sp. | Pulau Langkawi, Malasia | _ | _ | _ | _ | 118.03 | _ |
| Jayaraju, N., 2009 | Porites andrewsi | Tuticorin coast, India | 48.25 | _ | 8.53 | _ | 2.51 | _ |
| This study <i>Porites</i> sp. <i>Porites</i> sp. | Douitosom | VI I Island Days Bay Chine | 41.38-226.40 | 74.40-411.24 | 0.79-5.38 | 1.46-9.83 | 0.02-22.28 | 0.04-34.20 |
| | i ornes sp. | rites sp. XLJ Island, Daya Bay, China | $(78.54)^{a}$ | (142.46) ^a | (1.77) ^a | $(3.27)^{a}$ | $(3.57)^{a}$ | $(5.58)^{a}$ |
| | Paritas sn | DLJ Island, Daya Bay, China | 14.41-313.89 | 26.61-580.36 | 0-8.62 | 0.01-16.21 | 3.35-31.59 | 5.34-49.02 |
| | i ornes sp. | Des Island, Daya Bay, Chilla | $(63.44)^a$ | (120.01) ^a | $(1.50)^{a}$ | $(2.88)^{a}$ | $(10.97)^{a}$ | $(17.72)^{a}$ |

^a Numbers in brackets are mean values.















