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## The study of Chemical Impacts on Coral Reef Ecosystems around Okinawa Island, Japan

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**P23****The Study of Chemical Impacts on Coral Reef Ecosystems around Okinawa Island, Japan**

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The impact of chemicals such as organochlorine pesticides (OCPs), Polychlorinated Biphenyls (PCBs), Organotin (OT), Heavy Metals and Mercury on coral reef ecosystem is not well understood but some of these substances can have detrimental effects on the environment as well as humans. In addition, owing to the global warming and environmental change, coral reefs have been under a serious threat of degradation in the world. The focal points our research group are 1). Determination and elucidation of the impacts of chemicals (OCPs, PCBs, OT, Heavy Metals and Mercury) on aquatic, coastal and marine environment in Okinawa, 2). Analysis of organic carbon production of biological community in coral reef at Sesoko Island, Okinawa, 3). The study of Plutonium (Pu) Isotopes recorded in the growth band of Sclero sponge and 4). Geochemical studies of coastal hydrothermal activity at Taketomi and Okinawa Islands.

The contamination of organochlorine pesticides (OCPs) from the selected rivers in Okinawa Island was investigated to estimate the current status of pollution in water, sediments and plants in these rivers. Aja River, Asato River, Houtoku River, Kokuba River and Okukubi River were selected for this study. The concentrations of the total pesticides were the ranges of 0.94 – 231.8 ngL<sup>-1</sup> in river waters, 0.006 – 191.6 ngg<sup>-1</sup> (dry weight) in river sediments and 0.001 – 55.8 ngg<sup>-1</sup> (dry weight) in plants. Among the OCPs, the  $\Sigma$ HCB of  $\alpha$ -BHC,  $\beta$ -BHC and Aldrin were the common detected compounds in river water. The  $\alpha$ -BHC, Aldrin and Dieldrin were the most frequent detected compounds in river sediments and  $\alpha$ -BHC and Dieldrin were the common OCPs detected in plants. Aldrin, Dieldrin and  $\Sigma$ HCB were in abundance. Various contamination patterns between the selected river water, sediments and plants were observed. Aja, Asato and Houtoku were contaminated with  $\alpha, \beta, \delta, \gamma$ -BHC, Aldrin and Dieldrin (water and sediments) whereas the main OCPs in Kokuba River and Okukubi River was Dieldrin (plants).

Distribution, behaviour, composition and possible sources of PCBs in the marine environments around Okinawa Islands were also studied. Seawater samples were collected from seven points of open ocean including some points in the East China Sea and in the

Pacific Ocean. In coastal areas around Okinawa Island, six sea water and ten sediment samples were analysed. The total PCBs concentrations ranged  $0.05 - 0.25 \text{ ngL}^{-1}$  open water,  $1.59 - 2.48 \text{ ngL}^{-1}$  in coastal waters and  $0.32 - 128.7 \text{ ngg}^{-1}$  (dry weight) in coastal sediments. The total PCBs concentrations in coastal waters were relatively higher than that of open ocean. Also, the PCB levels in the coastal sediments were more than three orders higher compared to both open ocean and coastal sea water samples. In the water column, PCB level were increased with the depth in the open ocean.

Organotin compounds (OTCs) were investigated in seawaters and sediments from marine environments around Okinawa Island. The levels of OTCs detected in seawaters were MBT (mono-butyl tin);  $0.44 \pm 0.75$  (mean  $\pm$  SD), DBT (di-butyl tin);  $1.32 \pm 2.7$ ; TBT (tri butyl tin);  $0.72 \pm 2.9$  MPhT (mono phenyl tin);  $0.04 \pm 0.42$ , DPhT (di phenyl tin); 0.007 and TPhT (tri phenyl tin);  $0.013 \text{ ng (Sn) L}^{-1}$  ( $n = 30$ ). The maximum concentrations of OTCs were detected in Itoman port samples. The concentrations of tri-organotin (TBT and TPhT) showed a significant correlation between sediments and seawaters collected from Itoman port; TBT ( $r^2 = 0.59$ ;  $p < 0.01$ ) and TPhT ( $r^2 = 0.72$ ;  $p < 0.01$ ), ( $n = 10$ ) this suggests that they are of same origin. The TBT and TPhT in most port areas were above the threshold level ( $1 \text{ ngL}^{-1}$ ) and Environmental Quality Target (EQT)  $1 - 2 \text{ ngg}^{-1}$  of TBT for seawater and sediments respectively.

In addition, the distribution of Heavy Metals (Zn, Cd, Cu, Fe, Mn, Co, Ni and Pb) was investigated in surface sediment samples from Naha Port, Tomari port and Nakagusuku bay in Okinawa Island. The total metal concentrations in the samples were in the range of Mn ( $155 - 1840 \text{ mgkg}^{-1}$ ), Zn ( $86 - 2910 \text{ mgkg}^{-1}$ ), Pb ( $29 - 460 \text{ mgkg}^{-1}$ ), Cu ( $0 - 945 \text{ mgkg}^{-1}$ ), Co ( $14 - 204 \text{ mgkg}^{-1}$ ), Ni ( $0 - 240 \text{ mgkg}^{-1}$ ), Fe ( $9650 - 11400 \text{ mgkg}^{-1}$ ) and Cd ( $0 - 2 \text{ mgkg}^{-1}$ ). The concentrations of the heavy metals were found to be higher at Tomari port followed by Naha port and then Nakagusuku bay. A comparative study with the background levels of heavy metal content in the terrestrial soils showed a possibility of anthropogenic pollution of heavy metals such as Zn, Pb, Cu, Co and Ni at Naha port, Tomari port and Nakagusuku bay. The major elements analyzed showed a concentration ranges of Ca (1- 35%), Na (0.1 – 4 %), K (0.4 – 2%) and Mg (0.1 – 4%) and they were found to be higher at Nakagusuku bay as compared to Naha port and Tomari port.

Another known environmental threat was the outbreak of Mercury (Hg) poisoning contamination of Minamata Bay by an acetaldehyde plant and the poisoning of bread in Iraq in grain seeds had been treated with organomercury fungicides. Relatively high mercury concentration was reported for underground water in central area of Okinawa Island. Analytical result showed that mercury concentrations in groundwater were ranged from N.D –  $782 \text{ ngL}^{-1}$  or inorganic mercury and  $2 - 1112 \text{ ngL}^{-1}$  of total mercury at central area of

Okinawa. Ground water samples contain relatively high mercury concentration than seawater precipitation water samples.

In order to understand the present state of coral reefs and predict the future change, it is important to study the relationship between the global environmental change and the community metabolism in coral reefs. Thus we introduce a model to estimate the organic and inorganic carbon production rate of coral reef ecosystem under the natural water flow system, and present the results for a six year period. Therefore we came up with the results showed that the community metabolism was calculated by the water flow model and was within the range of the other coral reefs. Net Primary production was lower than zero during summer because of high respiration rate of benthic metabolism. This suggests that the Sesoko coral reef ecosystem has a significant seasonal variation that is autotrophic during winter and heterotrophic in summer. The results indicate that the water flow box model can be used for the estimation of community metabolisms in natural reef environment and applied for the long-term monitoring of the reef ecosystem.

We also investigate in the marine environment (mainly  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  isotopes) for the last decades, using a several centimeters of sclero sponge samples.  $^{240}\text{Pu}$  and  $^{239}\text{Pu}$  contents of skeletons were measured by MC-ICP-MS. The results showed that seasonal variation was clearly shown in the X-Ray radiograph and  $^{239}\text{Pu} / ^{240}\text{Pu}$  ratio of carbon skeleton showed a 0.22 – 0.17. The  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  concentration was peaked in 1945 – 1960 band ( $0.17 \text{ ngL}^{-1}$  and  $0.78 \text{ ngL}^{-1}$ ) and both showed similar behaviour decreasing from 1945 to 2000 ( $0.007 \text{ ngL}^{-1}$  and  $0.04 \text{ ngL}^{-1}$ ). This showed the effect of scavenging. It is known that  $^{239}\text{Pu} / ^{240}\text{Pu}$  atom ration of fallout depends upon the specific weapons device design and test fields. So, measurements of  $^{239}\text{Pu} / ^{240}\text{Pu}$  atom ratio in sclero sponge showed that the Pu fallout behaviour in the sea neat Miyako Island for the last 50 years.

Our last investigations was to examine and compare the hot springs and considered why both hot springs have been there in Onna village at northern part of Okinawa Island and one in Taketomi Island. Hot spring water and gas are blowing off from the inside of the hollow and around it. On the above hot spring areas, sediment like the bacteria-mat has been observed. There is no clear volcanic activity in the arc axis of central and southern part of the Ryukyu Islands. However there is hydrothermal activity like the Taketomi submarine hydrothermal activity. But the hear source and circulation process of these hydrothermal activity are not understood well. The Taketomi Island submarine hydrothermal activity has been focused in relation to the Iriomote Island swarm earthquakes.

The results obtained by our research group will be briefly discussed in this presentation.