D-3 Study on the Deterioration of Marine Environment Due to the Loadings of N and P and Silica Decline in the Global Aquatic Continua (Abstract of the Final Report)

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1. Introduction.

Anthropogenic loading of nitrogen (N) and phosphorus (P) have caused the aquatic eutrophication globally. Furthermore, it was pointed out recently that the cycle of silicon (Si) should be considered in the context of the "silica deficiency hypothesis" as follows[1),2),3)]. The increase of still waters from hydraulic alterations and elevated N and P loadings enhance the growth of freshwater diatoms, which convert DSi, supplied by the natural weathering of silicate minerals, to biogenic silicate (BSi). The BSi eventually sinks to the bottom and is effectively removed from the system. The consequent reduction of DSi in waters flowing downstream lowers its ratio relative to other nutrients in the coastal seas, causing the dominant phytoplankton species to shift from diatoms to non-diatom species. The former algae require Si to form their frustules. The latter algae, which are nonsiliceous, include the dinoflagellates and other flagellates, whose blooms sometimes cause harmful or nuisance phenomena such as massive fish kills, poisoning of shellfish, and other environmental problems. The environmental changes related to this hypothesis have been reported from several systems composed of the watersheds and coastal seas (Regions 3. to 7. in Fig.1). In spite of its importance, this hypothesis is accompanied by some scientific uncertainties and lacks the sufficient data especially in Asia, where economies are growing rapidly and yet the rate of the supply of DSi is higher due to the monsoon compared to Europe. On the other hand, UNEP has implemented the NOWPAP region (the seas surrounded by Japan, China, Korea, and Russia, see Fig.1) and one of its targets is to evaluate the river and direct inputs of pollutants to the marine environment, to which his study will contribute in the near future.

2. Research Objective

To verify this hypothesis based on the field data obtained in monsoon Asia and make appropriate output to the environmental policy making on global aquatic systems, we organized the following three sub-themes (hereafter referred to as S-1, S-2, S-3) and sub-sub-themes (abbreviated as Ss) under S-2 and S-3 covering this inter-disciplinary problem.

As an experimental field, we selected an aquatic continuum composed of the Lake Biwa (a natural lake assumed to be a large dam reservoir), Yodo River and Seto Inland Sea of Japan (hereafter referred to as BYS-system, Fig.1) based on the reasons as follows: i) this issue would be significant in the Asian countries because of the rapid growth of industry; ii) if this hypothesis were verified in Japan, whose natural conditions are rather of less likelihood of silica deficiency, it would prove the global significance of the hypothesis; iii) Japan experienced both of the rapid economical growth in 1960s and the regulation of loadings in the 1980th, which will be advantageous for bi-directional evaluation the response of the marine environment to the socio-economic changes; iv) we could evaluate the effects of silica deficiency considering the gradient of anthropogenic effects, which has been proved east-high and west-low. Also, the Shinano-River system was selected to contribute to the UNEP-NOWPAP Program.

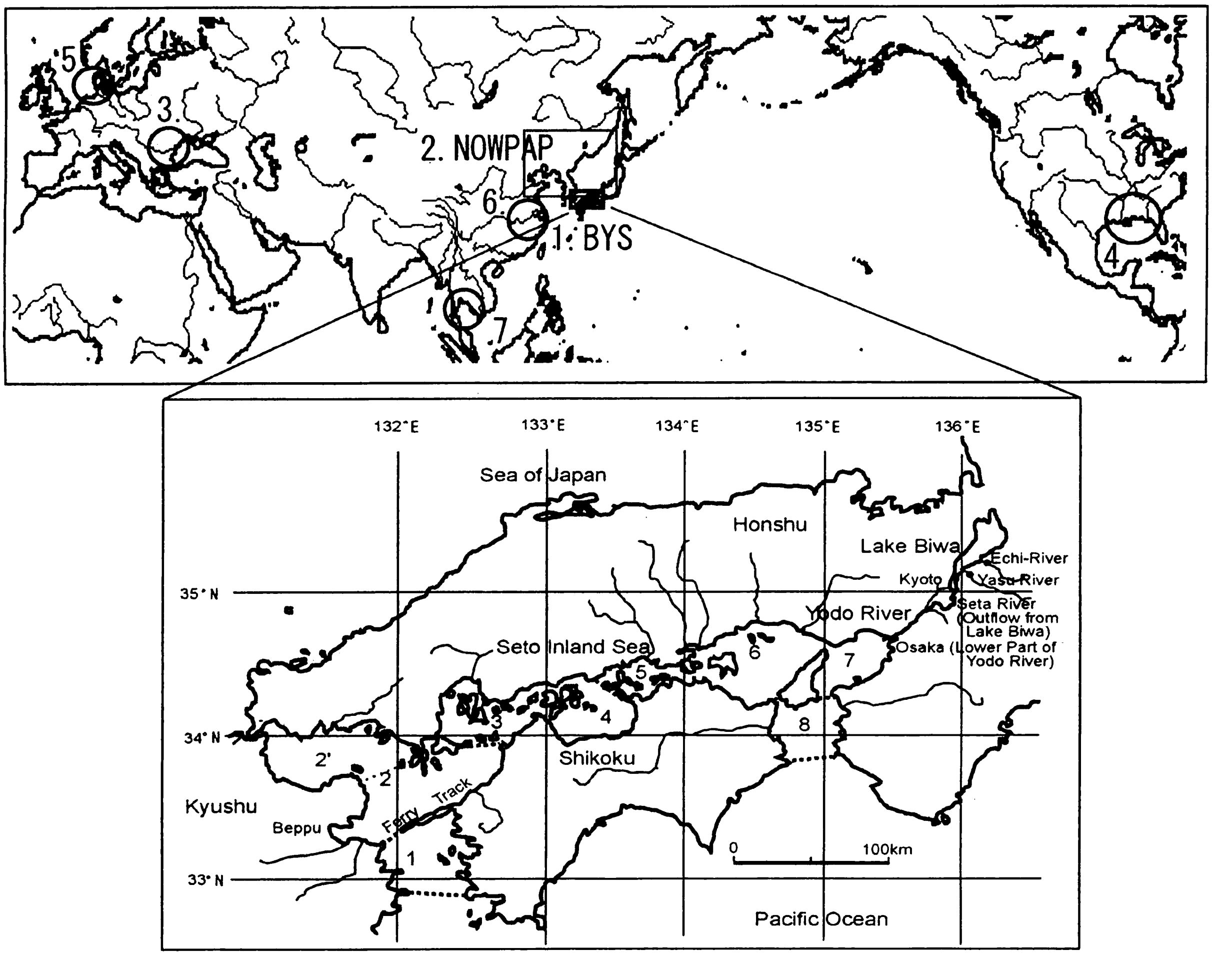

Fig.1 Upper figure: Locations of the regions from which silica-related environmental issue has been reported (Region 3. to 7. in the upper figure), the BYS-system, and the NOWPAP Region. Lower Figure: Map of the BYS-system with the ferry route along which sea surface nutrients were monitored.

3. Research title, organization (in the parenthesis), method and result of each theme

S-1: Comprehensive analysis on the marine response to the N, P and silica inputs

(National Institute for Environmental Studies)

The long-term biogeochemical trends in the BYS-system were analyzed with the existing data and our own measurements of Seto Inland Sea using ferry boat[4]. The results showed that Lake Biwa acted as a major sink for DSi, especially in the period of rapid economic growth, possibly depending on the change of P discharge. Also, the marine region neighboring the mouth of Yodo River acted as the sink of DSi because of the direct loading of N and P from land. Its effect on the relative dominance among algal groups in the sea could not be explained by simple stoichiometric arguments. Instead, it was necessary to define a control volume near the estuary of Yodo River where high levels of N and P and effluent Si enhanced diatom bloom, even though the Si/N ratio was lowered in the upstream reservoir. Si-depleted waters were then exported from this control volume to other parts of the sea, where they caused DSi and diatoms to decline. This speculative theory was confirmed by the time-series measurements using ferry, which showed the ratio of diatom biomass was higher in the summer with higher rains (2003) than the drought summer (2002). One apparent contradiction to the hypothesis is that HAB appeared in the Seto Inland Sea in summer, where DSi/DIN ratio is rather higher due to the summer precipitation. This contradiction to the hypothesis may be explained by that the major portion of diatom sinks in the end of spring bloom due to the lack of DSi and never rises to the upper layer until the autumnal overturning while the dinoflagellates can migrate between the nutrient-rich lower layer and the upper layer and grow there. These ideas fit other regions in the world such as the area off the mouth of Mississippi river (Region 4 in Fig.1), where the silica deficiency hypothesis cannot be directly applied.

S-2: Study on the Silica Sink in the Land Water and Watershed

Ss-2.1: Biogeochemical study on the silica cycle in the rivers and lakes

(The University of Shiga Prefecture)

The process of change in silica (DSi) caused for a biological factor was estimated in detail in the context of the relation among the watershed, rivers and Lake Biwa, which may act as a large reservoir causing the silica sink. The distribution and the process of change in concentration of DSi were investigated in Lake Biwa and rivers in 2002. In the result, it became clear that Lake Biwa where the residence time is long and the water depth is deep functions as the silica sink. Furthermore, it was found that the concentration of DSi is dependent on the geological factors and that the DSi discharge depends on the variation in the rate of water discharge affected critically by the rainfall events rather than the variation of its mean concentration, that is, the DSi discharge during a flooding is equivalent to several times of that in the time of normal water revel.

It is showed from the study in 2003 that the ratio of DSi to total Si ranged from 74 to 96 % in a river flowing into Lake Biwa and that the ratio of biogenic silica (BSi) and colloidal silica (CSi) to total silica ranged from 2 to 8% and 1 to 8%, respectively. The concentration of BSi was distributed similarly to the concentration of CSi in Lake Biwa, that is, their concentrations were high in epilimnion and metalimnion. In the bottom of Lake Biwa, it was found that these are a large quantity of BSi in the frustules of dead diatoms. These results indicate that the one part of BSi formed by diatom recurred to DSi through CSi within a period of its decomposition and sedimentation. The rest was reserved in the bottom sediment.

The sinking flux of BSi in Lake Biwa was estimated using sediment traps from December 2004 to February 2005. The sinking flux of BSi ranged from 453 to 1091 mg Si m^{-2} d^{-1} at 30 m depth and 141 to 265 mg Si m^{-2} d^{-1} at 70 m depth. The sinking flux at 70 m depth was low in December and high in February. On the other hand, the sinking flux at 30 m depth was low in February and in high December. This result shows that a large quantity of DSi is removed from water column in circulation period (February) because of rapid sedimentation of diatom frustules. It is considered from these studies that the scale of silica sink in Lake Biwa is determined mainly by biological (the utilization of DSi by diatom) and physical (the formation and loss of stratification) actions in lake inside.

Ss-2.2: Study on the silica sink in the dam reservoirs and its effect to the NOWPAP-Region

(Shinshu University)

To verify the silica deficiency hypothesis based on another dimension than that of the BYS-continuum, this sub-theme analyzed the Shinano River system, which consists of two tributaries, the Sai River (many dams have been constructed) Chikuma River (number of dams are smaller). Monthly monitoring of inorganic nutrients and related ions for 30 months from August, 2002 showed that the average DSi concentration of Chikuma River was ca. 1.8 times higher than that of Sai River suggesting the difference in the geological factors of these watersheds but no strong evidence on the effect of dams. In the case with less precipitation (residence time of water in the dam lake is longer than usual), DSi and DIP were lower in the downstream of Ikusaka Dam than in the upstream and the ratio of the depressions of two components are analogous to the Redfield ratio. Therefore, such decreases of DSi and DIP may be due to the absorption of freshwater diatoms. Also, in order to determine BSi and LSi separately, X-ray diffraction and NMR spectroscopy have been developing along with a conventional method (DeMaster method). These results were included in the National Report to the UNEP-NOWPAP in the context of the research activity on the river and direct input of contaminants into the NOWPAP region (Japan Sea).

Ss-2.3: Modeling of N and P discharge and silica sink in the catchments

(Okayama University)

Spatial distribution of silica and phosphoric acid in the Yodo River basin are compared with those in 1950s. Total phosphorus in river water is decreasing after 1970s at developing stage of industry, however, there is no major change from 1950s in DSi distribution. The highest DSi concentrations are observed in rivers around the South Basin, including the Yasu River. Measured silica concentrations are weighted by discharges and averaged into 178 μM, while it is only 33 μM in the out-flowing Seta River. The 80% of the gain is kept in the stems of reed and rice, cell wall of diatoms and their cists and detritus in the muddy bottom. The model is divided into the parts up- and down-stream of the lake, and the latter requires silica and discharge, combining into the flux. Reeds and rice straws release BSi silica bathed in a bottle of pure water. DIP and Chlorophyll-a are decreasing, while DSi and T-N are increasing in the hypolimnion of Lake Biwa. The facts of the watershed are considered and reflected on the synoptic basin model to describe hydrological and hydraulic aspects and seasonal change of the river basin, as well as cascade tank runoff model to distinguish subsurface runoff components from the surface one and to estimate the river water quality. Three-layered tank model is applied to major tributary basins with stream orders higher than three. The runoff process is compared with the annual hydrograph of 1991, and model parameters are determined, then quality analyses are made for 2002 to 2004 by considering both domestic and agricultural waste waters. Measured silica points were checked by the tank model for entering rivers into Lake Biwa, where fluctuations in silica are calculated at the downstream. Silica in the Uji River downstream the lake is lower and those in the tributaries, the Kizu and the Katsura Rivers, are higher than in the main river. The spatial pattern is compared between calculated and measured ones. Silica is a special staff, contained in tap water as much as in river water, added domestic silica to waste water. It is also released into rivers from stems of rice and reed in fields. That is why the flux path of silica is not single but possible in surface and subsurface runoffs. The estimated silica is kept within the observed range. Different weather conditions are tested for 2002 to 2004 and silica flux is checked in the coastal ecosystem model. Estimated silica range downstream is determined by discharge fraction of the main river with low DSi and two tributaries with the higher concentration.

S-3: Evaluation of effect of silica deficiency on marine ecosystem.

Ss-3.1: Evaluation of silica deficiency by laboratory and in situ experiments

(National Research Institute of Fisheries and Environment of Inland Sea)

In order to assess the effects of decrease in DSi loads on coastal ecosystem, spatial distributions of nutrients and chlorophyll *a* concentrations were investigated in Osaka Bay (eastern part of the Seto Inland Sea, Japan). Additionally, growth responses of diatoms and flagellates were examined in mixed cultures under phosphate- and silicate-limited conditions. The nutrient concentrations were generally high in Osaka Bay, suggesting that the growth of natural diatom communities in this Bay was not limited any nutrients. The most part of silica flowing into Osaka Bay was consumed by diatoms in the inner part of the bay, suggesting that silica is trapped within the inner part of the bay. Our experimental data using two diatoms (*Chaetoceros dydimum*, *Thalassiosira rotula*) and two flagellates (*Heterosigma akashiwo*, *Isocrysis galbana*) indicated that the succession from diatoms to flagellates occurs at a silicate concentration of 2-3 μmol L^{-1}, and that the phytoplankton community structure is affected by the phosphate concentrations.

Ss-3.2: Evaluation of silica deficiency by N, P and Si-dependent ecosystem model

Kyushu University

This sub-theme constructed the numerical ecosystem models with two boxes. The results for Osaka Bay, into which the Yodo River is flowing, showed that the condition for the algal growth is P-limiting rather than Si-limiting. Also, the results suggested that the main reason why the occurrence of non-diatom red tides dominated in early 1990 but that by diatom in late 1990 is due to that non-diatom phytoplankton with higher half saturation constant of DIP than diatoms could not increase in late 1990 because DIP concentration had decreased due to the regulation of phosphorus use on land.

5. Discussion and Conclusions

From the results under each theme, we could construct a scenario on the sequence of phenomena related to the silica decline: The Lake Biwa (assumed large reservoir) and the coastal sea with intense direct loading of N and P function as two major sinks of DSi. These sinks affect the ratio of DSi relative to DIN in the eastern part of the Seto Inland Sea. The limiting factor for the growth of phytoplankton in the lake is basically P, which controls the intensity of the sink of DSi. Also, a dam lake in the Shinano River, whose residence time of water is shorter than that of the Lake Biwa, showed a weak sink of DSi depending on the time-dependent flow rate of water. Therefore, the nature of the silica trap seems to be common to the still water body with supplies of certain amount of N and P. Based on the analysis of existing data, the water quality of the averaged Japanese rivers shifted in the direction of the higher-DIN and lower-DSi.

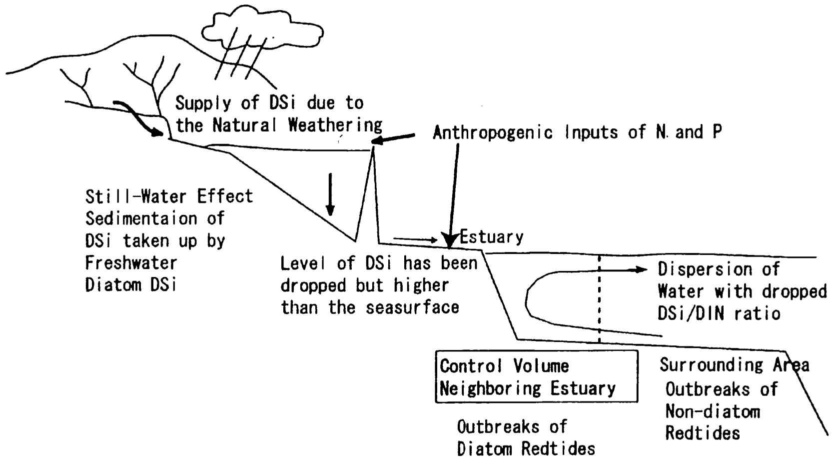

Fig.2 Schematic diagram of the silica deficiency hypothesis

The results from the mixed-culture experiments showed the shift of dominant species shift from diatom to flagellates when DSi is around 2 to 3 μmol L^{-1}. However, the observed of algal composition did not straightforwardly fit the classical silica deficiency hypothesis. One point is that in Osaka Bay, which receives the DSi-dropped water from Lake Biwa and DSi/DIN is the least in the Inland Sea, diatom-induced red tides predominated. This is explained by the following speculation. In the region neighboring the mouth of the river (Fig.2), the absolute supply of DSi and direct discharge of N and P from land enhance the fast growing diatom because none of N, P and Si limits their growth even if the relative ratio DSi/DIN has dropped in the upstream lake. The DSi/DIN ratio in the waters dispersing from this region has become lower due to the uptake of diatom and allows the appearance of non-diatom species in the other part of the sea.

Geological factors and high precipitation cause Japanese rivers to have naturally higher DSi concentrations than averaged values for European rivers. In particular, the monsoon characteristics tend to raise the DSi yield in summer, showing rather a lower likelihood of silica deficiency compared with the situation averaged over the world. Despite these conditions, the ecosystem of BYS continuum is sensitive to the variation of DSi. Therefore the silica deficiency hypothesis may hold true in many aquatic continua in the world — both currently and potentially.

6. Reference

1) Billen, G., Lancelot, C. and Meybeck, M: N, P, and Si retention along the aquatic continuum from land to ocean, in Mantoura, R.F.C. *et al.* (Eds.) *Ocean Margin Process in Global Change*, 19-44, Wiley (1991).

2) Ittekot, V., Humborg, C. and Schäfer, P. (2000) Hydrological alterations and marine biogeochemistry: a silicate issue?, *BioScience* 50, 776-782.3)

3) Humborg, C., Ittekot, V., Cociasu, A. and Bodungen, B. (1998) Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure, *Nature* 27, 385–388.

4) Harashima, A. *et al.* (1997) Monitoring algal bloom and related biogeochemical changes by a flow-through system deployed on ferries in the adjacent seas of Japan, in Kahru, M. and Brown, C. B. (eds.) *Monitoring Algal Blooms*, 183-213, (Springer, 1997).