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# EUTROPHICATED SEDIMENT REMEDIATION USING SHELL FRAGMENT AS REGIONAL UNUSED RESOURCES FOR NUTRIENTS ELUTION CONTROL

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**ABSTRACT:** Dominant species of Aoko, *Anabaena*, has a “function of nitrogen fixation from air”, so if there is even phosphorus in water, they can multiplicate explosively. This study aimed the removal of phosphorus by shells of regional unused resources as eutrophication countermeasure in Hasunuma Seaside Park Pond. As result, sprinkling crushed shells was essential to the removal of phosphorus and the increase control of phytoplankton such as *Anabaena spiroides*. Inhibition rate of phosphorus showed a high percentage with much quantity of dispersion. At the N/P ratio, all dispersion system showed the higher value in comparison with no-treated systems. Hardness showed a high percentage with much quantity of dispersion because of $Ca^{2+}$ was eluted into water from shell body. The dominant species of phytoplankton was changed to *Chlorella* sp. and the growth of the phytoplankton was controlled until fifth or tenth day by $Ca^{2+}$ eluted from shells fragment.

*Keywords: Shell, Regional unused resources, Phosphorus removal, Water quality, Brackish pond*

## 1. INTRODUCTION

In the lakes of Japan, the achievement rate of chemical oxygen demand (COD) or biochemical oxygen demand (BOD) of environment standard is lower than those of rivers and sea, and eutrophication is under progressing condition. Fig.1 showed secular change of the environment standard of rivers, sea and lakes [1]. It showed high achievement rate of 92.5% in the river and 78.3% in the sea, but that of lakes showed low value of 53.2%. As reason for this, lakes are closed environment, and the resources of nutrient salt are flow from rivers and elution from sediment. Many countermeasures against eutrophication have been suggested and carried out. But it is not effective because there are problem of cost and maintenance management. Lake Tega and Lake Inba of Chiba prefecture in Japan are one of the most famous eutrophicated lakes. They are tackling water environment repair of dredge and raw water transmission business [2].

As eutrophication countermeasure of lakes, there are physical method such as sediment transaction, introduction of water purification and the change of flow path of influent water. But it has problem of cost and maintenance management. Another countermeasure is biological method such as removal of fishes. But it has problem of the breakdown of ecosystem. Therefore, a new method is demanded to solute these problems.

## 2. MATERIALS AND METHODS

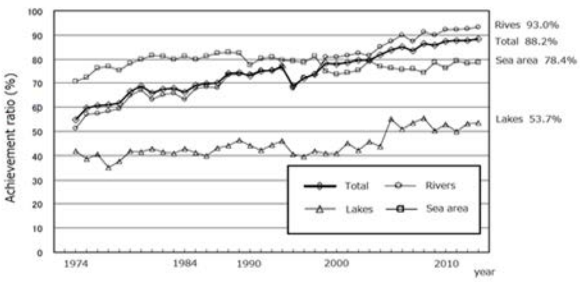


Fig.1 Achievement rate of environmental standards (COD, BOD) in lake, river and sea in Japan

### 2.1 Outline of Experimental Pond

Hasunuma Seaside Park Pond (Fig.2) in Sanmu city of Chiba prefecture locates at 350m inland from Kujukurihama coast. This pond is strong enclosed, and its surface area is about 10,000m², water volume is about 7,400m$^3$, the water depth is 0.74m in average. In past, a rental boat shop opened in this pond, but the problem of stink and deterioration of landscape occurred because Aoko occurred in every summer (Fig.3). Improvement works of drying in the sun and drainage work conducted, but Aoko occurred again in summer of next year [3].

Dominant species of Aoko at this pond is Anabaena spiroides (Fig.4). It has air nitrogen fixation ability. Therefore, they can multiplication explosively if there is enough phosphorus in water. The other side, many shells scattered in Kujukurihama coast on nearly of Hasunuma Seaside Park pond. Ca of the constituent parts of shell can adsorb phosphorus as formula (1) of below.

$$Ca^{2+} + HPO_4^{2-} + 3H_2O \rightarrow CaHPO_4 \cdot 3H_2O \downarrow \quad (1)$$

Shells are dumped as industrial wastes every year. Using these shells wisely, they can improve water quality and decrease industrial wastes. This study aimed the removal of phosphorus by physical adsorption and chemical combination with Ca eluted from shell fragments.

### 2.2 Regional unused resources

In this study, *Anadara broughtonii* (Fig.5) was supplied as a regional unused resources. It is clam that belongs to species Aroodia family Arcidae. These shells inhabit in low tide area and bottom mud of inner bay. As character of shell, it has about 42 radial ribs. And its blood is red for it has Erythrocruorin that similar to hemoglobin [4].

This shell was broken into 1-3mm size fragment (Fig.6). It sprinkled on the bottom mud of nutrients resources. Shells are scattered many in Kujukurihama coast of neighboring of Hasunuma Seaside Park Pond. And when its fragment sprayed on bottom mud, the surface of bottom mud looks bright by a reflection of the light.

### 2.3 Experimental Methods

Water volume in the microcosm test is generally 300-1,000 ml[5]. From this reason, clear glass container (volume: 470ml, height: 14cm, diameter: 7cm,) was used in this study. Mud sediment of 100g collected from the pond was put in the bottom of the container to become flat, and pond water of 380ml was poured without disturbing the sediment. Crashed shells were sprinkled on sediment mud. The microcosm system was cultured in incubator. Culture period was 20 days, and culture system is no-treated system and sprinkled systems of 5, 10, 20, 30, 50, 80, 90, 100g/m$^2$. Culture condition was 25 degrees(Celsius) in temperature and 2,400lux in illuminance (L/D = 12/12hr). Measuring parameters were T-P (total phosphorous), $PO_4$-P, T-N (total nitrogen), $NH_4$-N, $NO_2$-N, $NO_3$-N, COD, chlorophyll a (Chl.a), pH, DO, hardness (Ca+Mg), and phytoplankton. Phytoplankton flora was observed in every 5 day.

## 3. RESULTS AND DISCUSSION

### 3.1 Phosphorus removal

Fig.7 and Fig.8 showed the inhibition rate of T-P and $PO_4$-P. It showed high value because of there

Fig.2 Hasunuma seaside park pond

Fig.3 Aoko in Hasunuma Seaside Park pond


Fig.4 *Anabeana spiroides* (Aoko)


Fig.5 *Anadara broughtonii* (shell)


Fig.6 Crushed shells fragment

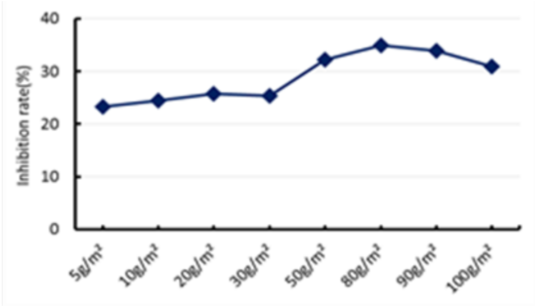


Fig.7 Inhibition rate of T-P in each microcosm

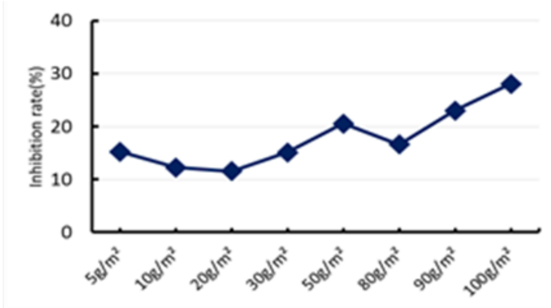


Fig.8 Inhibition rate of $PO_4$-P in each microcosm

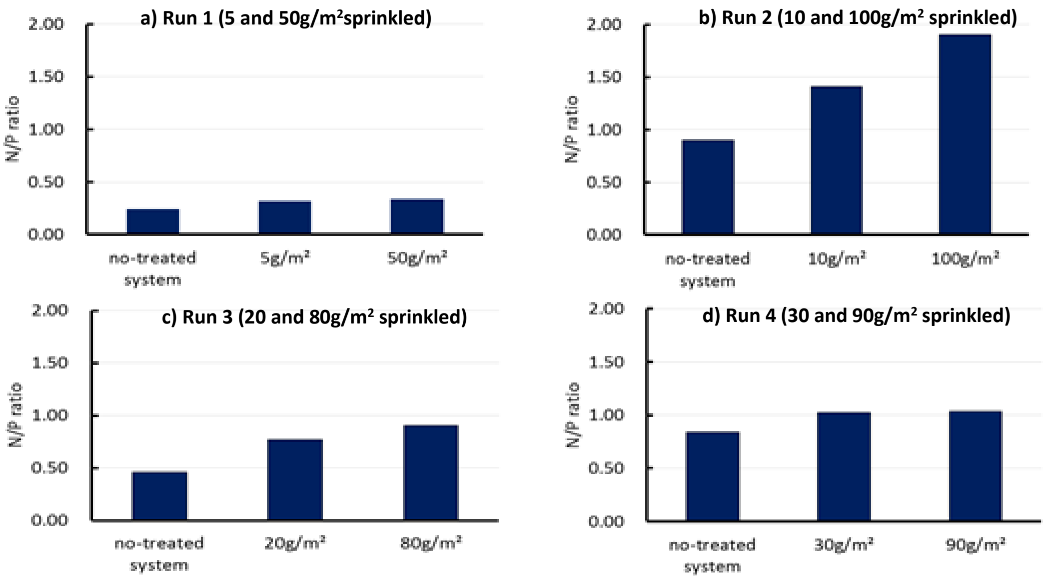


Fig.9 N/P ratio in each microcosm (20days after)

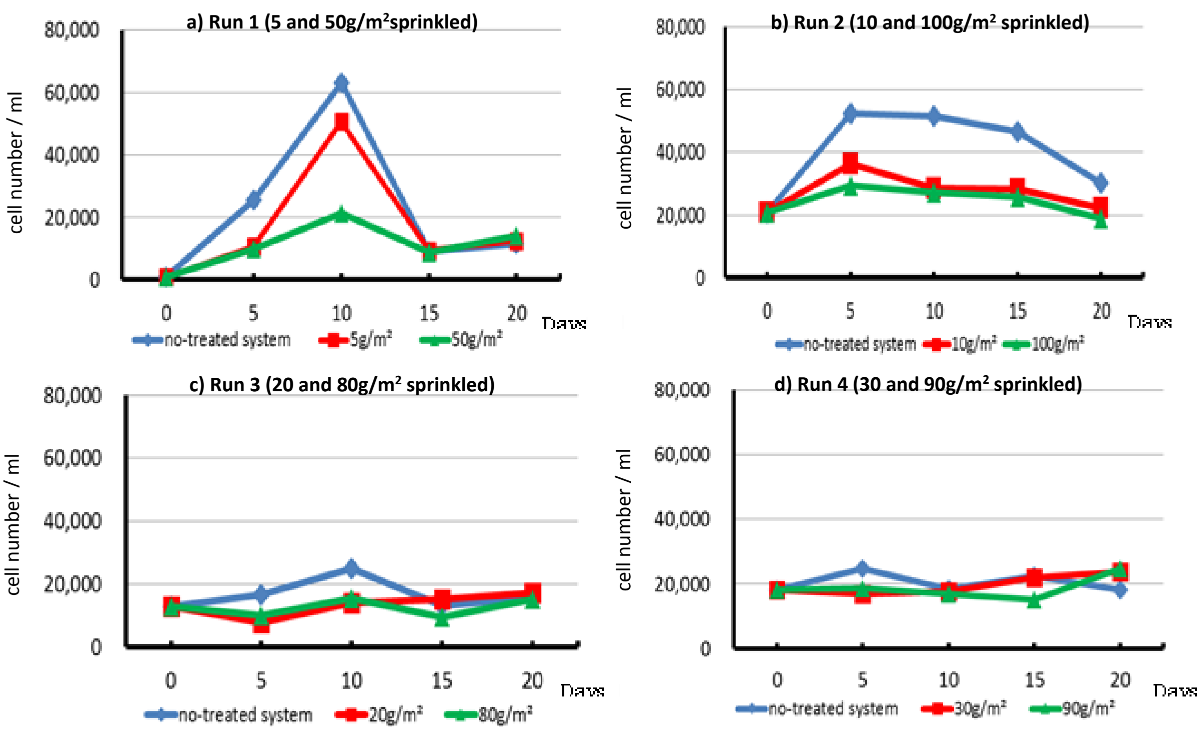


Fig.10 Total cell number of phytoplankton in each microcosm

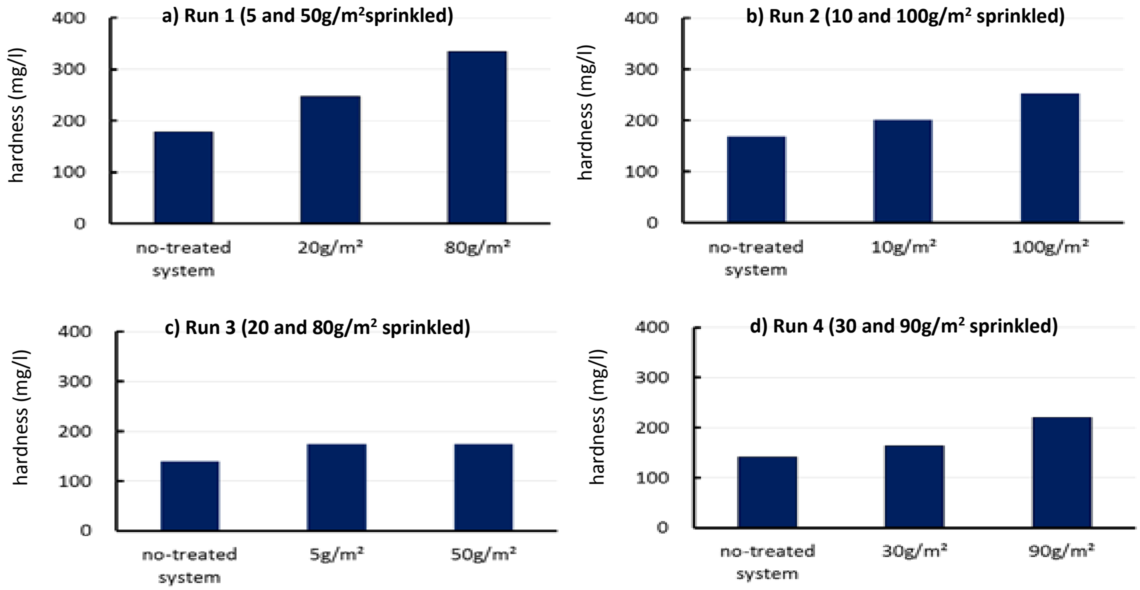


Fig.11 Hardness in each microcosm (20days after)

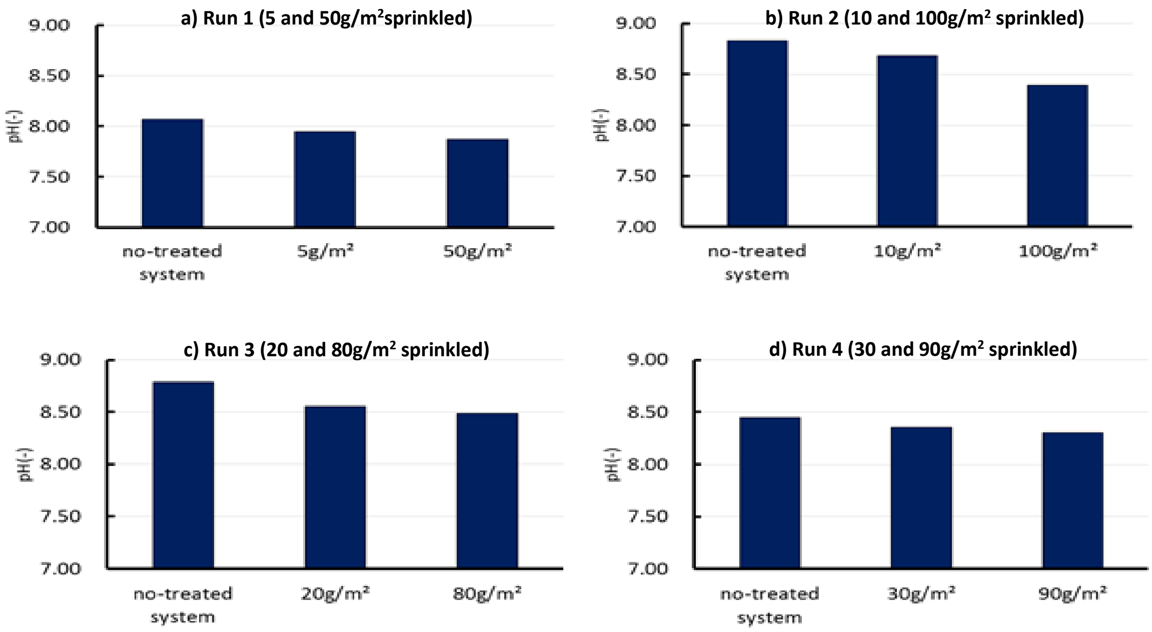


Fig.12 pH in each microcosm (20days after)

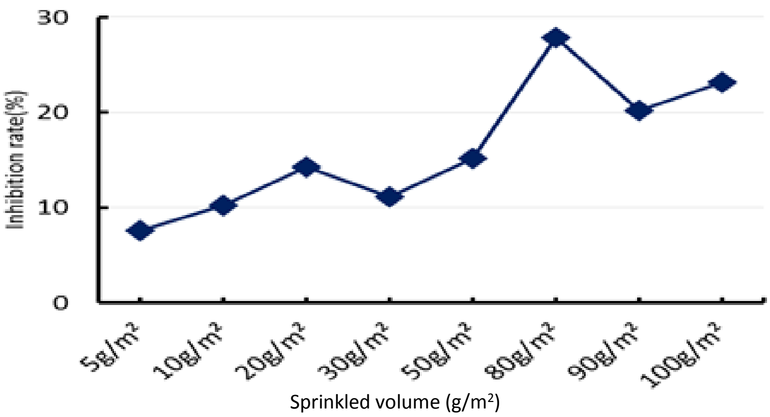


Fig.13 Inhibition rate of COD in each microcosm

was much sprinkled in volume. It was the highest inhibition rate of T-P: 34.9% and $PO_4$-P: 28%. In T-P, the inhibition rate became flat at sprinkled quantity of 5-30g/m² and 50-90g/m². The inhibition rate of phosphorus did not change between each quantity of dispersion.

The inhibition rate decreased at sprinkled quantity of $80g/m^2$-$100g/m^2$. As reason for this, the sprinkled shell fragments overwrapped each other, and this cause is the decrease of surface area.

The solubility product of shells in water can be described as formula (2) of below [6][7]. Therefore, combination adsorption quantity of phosphorus eluted from bottom mud and $Ca^{2+}$ eluted from shell fragments was particle. As this result, the mechanism of phosphorus adsorption in this study was considered as mainly physical adsorption.

$$[Ca^{2+}][CO_3^{2-}] = (3.6\times10^{-9})^2 \quad (mol/L) \quad (2)$$

### 3.2 N/P ratio in water

Fig.9 showed the N/P ratio in the microcosm. N/P ratio in all sprinkled systems showed high value than no-treated system. From this result, N/P ratio increased by $Ca^{2+}$ which adsorbed phosphorus and it changed to the direction of the proper N/P ratio from P excessive. However, N/P ratio is below 2.0 in all systems. Therefore, it was state of excessive phosphorus yet. The proper value of N/P ratio is about 10. In Lake Inba and Lake Tega in Chiba prefecture where well known as the most eutrophicated lakes in Japan, N/P ratio of these lakes are about 8.5 in summer [2]. However, N/P ratio in Hasunuma Seaside Park Pond of previous years was below 2.5[3], it was conditions of excessive phosphorus. In addition, *Anabeana spiroides* that dominant species of Aoko can breed if there is even phosphorus by air nitrogen fixation ability. Condition of phosphorus excess in Hasunuma Seaside Park Pond is serious problem.

### 3.3 Relationship between phytoplankton and regional unused resources

Fig.10 showed the daily variation of phytoplankton in microcosm system. The dominant species were *Chlorella* sp. in all systems. The population of sprinkled systems was less than no-treated system until fifth to tenth day. As reason for this, phosphorus concentration decreased by $Ca^{2+}$ that constituent of shell adsorbed phosphorus. By this, breeding of phytoplankton was controlled. Tsunami flowed in Hasunuma Seaside Park Pond by the Great East Japan Earthquake in March 2011, and breeding of *Anabeana spiroides* as dominant species of Aoko were controlled. But, water quality recovered to the state before the earthquake. Therefore, Aoko may occur again. In this study, sprinkled shells were effective to control phytoplankton that formed Aoko.

### 3.4 Hardness in water

Fig.11 showed hardness value in the each microcosm. It showed a high value so that there was much sprinkled volume. As this result, it was thought that $Ca^{2+}$ that a component of the shells eluted in water. When there is much quantity of $CO_2$, $CaCO_3$ which is constituent of the shell becomes easy to elute. In this study, quantity of photosynthesis by breeding controlled of phytoplankton accompany with sprinkle of shell reduced. By this, DO value becomes low of about 5mg/L. Therefore, the water becomes the anaerobic state, and it was thought that Ca eluted.

### 3.5 pH in water

Fig.12 shows the pH in each microcosm. pH is 8-9, and sudden change accompany with sprinkle of shells was not observed. As this reason, $CaCO_3$ eluted in water, it becomes formula (3) below.

$$CaCO_3 + 2H_2O \rightarrow Ca(OH)_2 + H_2CO_3 \quad (3)$$

Ca $(OH)_2$ is acidic. And $H_2CO_3$ is alkaline. By this, water quality becomes neutral, and sudden change of pH was not seen.

### 3.6 Relationship between COD inhibition rate and sprinkle volume

Fig.13 shows the inhibition rate of COD in the microcosm. It showed a high value so that there was much sprinkled in volume. $Ca^{2+}$ eluted from sprinkled shells, and it was combination with phosphorus which is nutrients, and breeding of phytoplankton was controlled. Therefore, organic matter in the water was reduced, COD inhibition rate was higher.

## 4. CONCLUSIONS

This study focused Ca which constituent of shells as the regional unused resources which was many scattering in Kujukurihama coast. It removed phosphorus by physical absorption and $Ca^{2+}$ that eluted from shells, and it aimed to improvement from eutrophication state of water. The results were as follows.

1) With sprinkling the shell as regional unused resources, phosphorus that eutrophication material by chemical combination and physical adsorption

of shells was controlled.

2) With sprinkling the shell, N/P ratio changed to the direction of the fair N/P ratio from P excessive. However, N/P ratio was below 2.0 in all systems. Therefore, it was state of excessive phosphorus yet.

3) COD inhibition rate was higher. Because $Ca^{2+}$ eluted by sprinkled shells, and it was combination with phosphorus which is nutrient salts, and breeding of phytoplankton was controlled. Therefore, organic matter in the water was reduced,

4) Dominant species of phytoplankton was *Chlorella* sp. in all system. The phytoplankton population of sprinkled systems was less than no-treated system until fifth to tenth day.

## 5. ACKNOWLEDGEMENTS

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