

OPTIMUM CONDITIONS OF OYSTER SHELLS AS MATERIAL COVERING SEDIMENT AND INHABITATION SIMULATION OF INTERNAL LOAD USING ECOSYSTEM MODEL

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ABSTRACT: A remediation program for a canal with water quality problem will be carried out in the future, and internal load from the bottom sediment can be new problem. Remediation measure against internal load was investigated by using oyster shells as covering material. So that shell-covered sediment experiments and numerical experiments were carried out. Pre-treatment such as graining and heating might be in vain, and non-heated shells of chip or powder size will be optimum. Properties of nutrient elution were also obtained at the experiments. Numerical experiment was investigated on reducing patterns against external load and internal load to evaluate the various remediation measures by using ecosystem model added shell-covered sediment model. Only shell covering might have the small effect of water quality improvement. Good water quality is expected to be archived in the long period by a combination of reducing external load and applying bioresources.

Keywords: Oyster shell, Shell-covering effect, Internal load, Ecosystem model, Simulation

1. INTRODUCTION

Areas lower than sea level tend to have the water quality problems due to water retention because water drainage can barely proceed by gravity in low-lying areas. Water quality has deteriorated in the main drainage canal that runs through K. Town, Mie Prefecture, Japan. Due to topography constraints drainage does not flow like a river in low-lying areas such as K. Town, so the town must depend on pumping machines. Aquaculture effluent containing feed residue from fish has been dumped into the canal in addition to agricultural effluent containing soil particles from paddy fields. A remediation program has been discussed and planned for a long time to improve the water quality. While this program will be carried out in the future, by then, the internal load from the canal sediment could be greater than the improvement to the water quality in the canal.

Changes in the domestic production of oyster shells in the last decade are shown in Fig. 1 [1]. The weight ratio of oyster shells divided by oysters is 0.8 according to [2]. Shell weight was estimated by multiplying the oyster weight by the ratio of 0.8. The average annual production of oyster shells amounts to approximately 160,000 tons within Japan. There is a yield of 4,000 tons of oyster shells per year in Mie. Disposing the shells, which are industrial waste, is a major matter in any other producing areas as well as Mie. The aftermath of the 2011 Tohoku earthquake and tsunami led to a considerable decline of oyster shells containing Miyagi's production as shown in Fig.1. However, the disposal of oyster shell still remains a large problem.

Uses for oyster shell have been studied to improve various bad environments. First, improving bottom sediment was investigated. It was found that oyster shells adsorb the hazardous sulfated hydrogen in river-mouth mud [3]. Oyster shells decrease the sulfide in brackish-lake mud as in [4]. Second, using oyster shells as material for purifying water was investigated. Oyster shells were immersed in water for agriculture, decreasing the total amount of nitrogen, especially ammonia nitrogen, in water [5]. Oyster shells were used in the process of changing ammonia nitrogen into nitrate nitrogen and denitrifying [6]. Last, oyster shells were used as material covering sediment. Sediment areas covered with oyster shells and without shells were set up in Lake Hamanako, and the concentrations over these areas were measured as in [7]. They showed that the sulfide concentration over the test area was a tenth of the concentration over the control area. Reference [8] measured the concentrations of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ over sediment covered with both shells and without shells in the laboratory. The sediments were sampled from the bottom of Lake Kojimako. The concentrations of the covered sediment were lower than those of the control. Reference [9] indicated that another kind of shells led to similar results. Almost all previous research was done in areas with brackish water and salt water. Thus, it will be necessary to investigate applications for freshwater areas.

It is important to evaluate the impact of sediment on water qualities in order to calculate these concentrations in water area. The nutrient exchange processes between sediment and its above water, especially sedimentation process and decomposition



Fig. 1 Changes of annual production of oystershell with time [1]

process of phosphorus, were focused and investigated. Elution of phosphorus was calculated by using the phosphorus elution model from sediment, then various remediation measures against phosphorus release from sediment were estimated [10]. However, it is not easy to fractionate phosphorus components in sediment for the modeling, and a simple elution model appears to be needed.

In this study, experiments on internal load from shell-covered sediment were carried out under various shell conditions in order to apply the oyster shells as material covering the sediment in freshwater areas, and the optimum condition for the pre-treatment of oyster shells was investigated. Furthermore, this was done on the assumption that oyster shells would be used as covering material in the main drainage canal, and how shell-covered sediment could impact water quality in the field was investigated. A shell-covered sediment model was added to a known ecosystem model, and numerical simulations were carried out. The essential results of shell-covered sediment experiments were used to consider the model parameters and simulation patterns.

2. METHOD

2.1 Method of numerical experiment

2.1.1 Calculation model

The main drainage canal in K. Town is T-shaped and is about five kilometers long water area. Water, especially rainfall runoff, flows into the main drainage canal though not only the upstream edge of the canal but also many branch drainage canals. Two drainage pump station are located at the other downstream edge of the canal. Besides rainfall runoff, water in the main drainage canal consists of agricultural effluent from paddies, treated water from wastewater treatment plants, and food factory effluent. The concentrations had a similar trend with each other in the main canal. Therefore, the entire

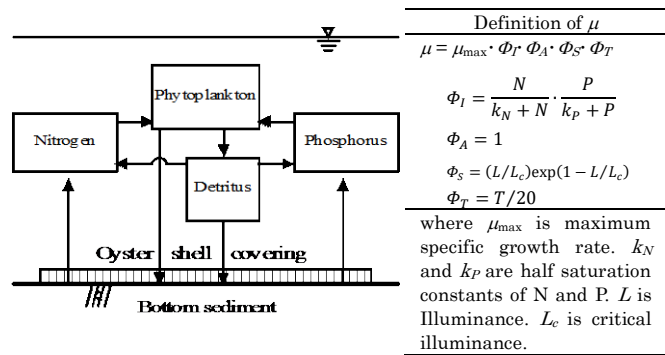


Fig. 2 Water quality and ecosystem model with oyster shell covering

main drainage canal was simplified as a single layer model with mean depth z .

The water quality and ecosystem model based on algal shown in Fig. 2 was used for analysis. It was added to this model that oyster shells covering the sediment inhibited nutrient elution from sediment. The model equations are four ordinary differential equations as shown in Eq. (1)-(4).

$$\frac{dA}{dt} = \mu \cdot A - k_d \cdot A - \frac{v_A}{z} A + \{\Sigma(A_{in} \cdot q) - A \cdot Q\} / V \quad (1)$$

$$\frac{dD}{dt} = r_D \cdot k_d \cdot A - \frac{v_D}{z} D - k_M \cdot D + \{\Sigma(D_{in} \cdot q) - D \cdot Q\} / V \quad (2)$$

$$\frac{dN}{dt} = -r_N \cdot \mu \cdot A + r_{ND} \cdot k_M \cdot D + (1 - \Phi_{inhN}) \frac{IR_N}{z} \theta_N^{T-20} + \{\Sigma(N_{in} \cdot q) - N \cdot Q\} / V \quad (3)$$

$$\frac{dP}{dt} = -r_P \cdot \mu \cdot A + r_{PD} \cdot k_M \cdot D + (1 - \Phi_{inhP}) \frac{IR_P}{z} \theta_P^{T-20} + \{\Sigma(P_{in} \cdot q) - P \cdot Q\} / V \quad (4)$$

where A , D , N , and P are concentrations of chlorophyll-a, detritus, nitrogen (N), and phosphorus (P) in main drainage canal, respectively. These variables are function of time t . Q is total influent discharge as shown in $Q = \Sigma q$, and q is individual influent discharge like rainfall runoff. k_d is death factor of phytoplankton. v_A , v_D are settling velocities of phytoplankton and detritus, respectively. r_D is conversion factor between phytoplankton and detritus. k_M is decomposition and mineralization constant for detritus. r_N , r_P are conversion factors between phytoplankton and nutrients N, P, respectively. r_{ND} , r_{PD} are conversion factors between detritus and N, P, respectively. Φ_{inhN} , Φ_{inhP} are inhibition ratios of N and P elution. IR_N , IR_P are

elution rates of N and P, respectively.

The time integration method of Eq. (1)-(4) was the fourth order Runge-Kutta method. The time step was set to be one day. It was supposed that the water volume V of the main drainage canal was constant in these equations. In low-lying areas, water such as rainfall runoff gathers through a hydraulically continuous lateral drainage canals. Drainage pumped at each downstream edge daily causes only a small flow in the main drainage canal, and consequently, a small fall in the water level rapidly returns to normal.

2.1.2 Input data for calculation model

Monthly input data used for the calculation are shown in Figs. 3 and 4. Shown are the discharges of various influents, chlorophyll-a concentrations A_{in} , suspended solids D_{in} , total nitrogen concentrations N_{in} , total phosphorus concentrations P_{in} , water temperature T in the main drainage canal, and the illuminance L around the field. These input data were determined by a committee [11] between April 2002 and March 2003, except for the illuminance. Illuminance data were quoted from a data book [12].

Waters influent into the main drainage canal consist of rainfall runoff from a basin, agricultural effluent from paddies and upland farms, treated water from the wastewater treatment plants, and food factory effluent. Each influent discharge q was monthly calculated on the basis of the water balance in the basin. Suspended solids SS were substituted for detritus concentrations D_{in} of each of the influent waters.

Rainfall runoff, calculated on the basis of rainfall, appears to flow into the main canal through the hydrological continuum of branch drainage canals. Since the daily drainage done by two pump stations pulls only a small volume of water into the main canal, the pollutant runoff coefficient could be great because the pollutant settles under slow water movement, and inflow loads associated with rainfall runoff were supposed to be zero for all water quality items.

Agricultural water supplied into the basin caused the agricultural effluent to discharge. The irrigation period was between April and August in K. Town. Agricultural effluent corresponds to almost all of the agricultural water supply and period. Inflow load associated with agricultural effluent was calculated on the basis of observed concentrations at paddies.

Since the wastewater treatment plants deal with household effluent, the plants have monthly constant discharges and regular concentrations. The inflow load was calculated by using constant discharges and observed concentrations.

Discharge of food factory effluent was incommensurably small value, as shown in Fig.3 (A). Furthermore, since the waste outlet of the food factory is very close to the pump station at the

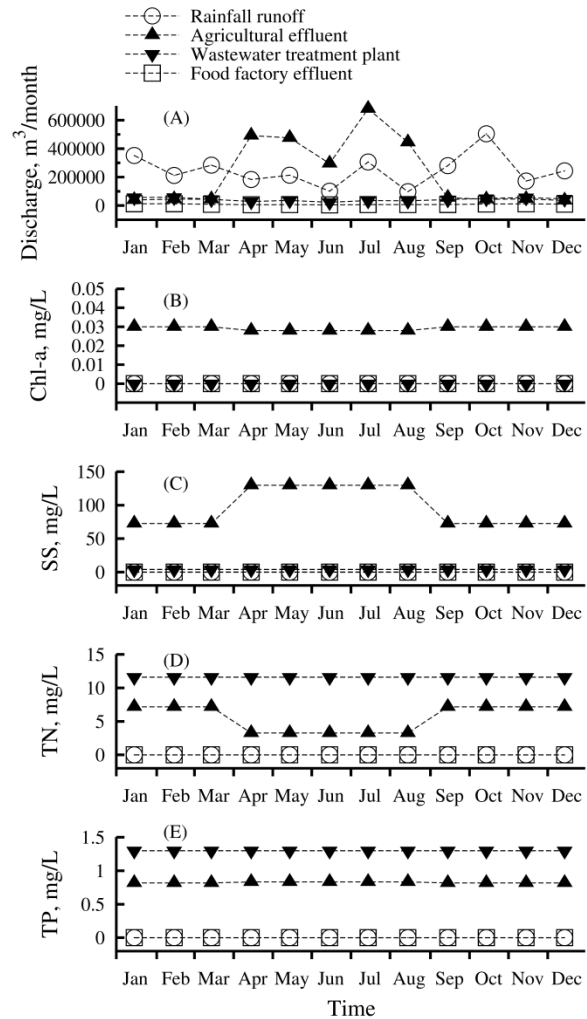


Fig. 3 Changes of influent discharges into the main drainage canal and their water qualities

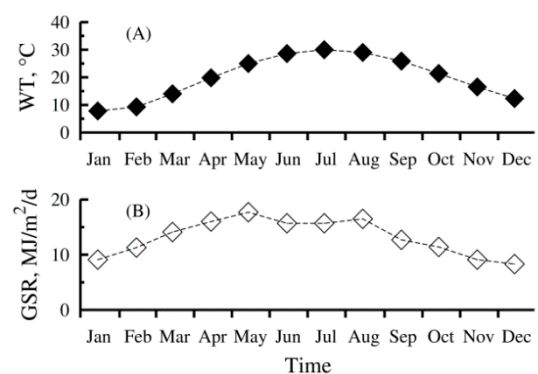


Fig. 4 Changes of (A) water temperature in the main drainage canal, and (B) amount of global solar radiation

downstream edge in the main canal, the effluent has no effect on the whole of the main canal. Consequently, all inflow loads for factory effluent were supposed to be zero.

Chlorophyll-a, total nitrogen, total phosphorus, and water temperature were determined in the main

Table 1 List of reduction ways of external load and internal load

External load		Internal load	
Reduction ratio	Symbol	Reduction ratio /inhibition pattern	Symbol
000% off	E-1	No remedy (000% off constant)*	I-1
025% off	E-2	Perfect dredging (100% off constant)*	I-2
050% off	E-3	Covering type 1 (stepwise decrease)**	I-3
-	-	Covering type 2 (linear decrease)**	I-4

*) Φ_{inh} 's patterns of N, P are the same as shown in Fig.5. **) Φ_{inh} s are different in N, P.

Table 2 Numerical experiment patterns

External load	Internal load			
	I-1	I-2	I-3	I-4
E-1	Run01	Run02	Run03	Run04
E-2	Run05	Run06	Run07	Run08
E-3	Run09	Run10	Run11	Run12

drainage canal. The observed date of the water temperature was fit as a five order polynomial equation, shown in Fig.4 (A), to be used for model calculation.

Instead of illuminance, the amount of global solar radiation was used to calculate influence function Φ_s . The monthly amount of global solar radiation shown in Fig.4 (B) was measured near K. Town [12].

2.1.3 Simple model equation for covering elution from sediment

Experimental equations for nutrient elution from sediment are often expressed as a function of water temperature T [13]. The author modifies and proposes new experimental equation Eq. (5) and (6) with inhibition ratio Φ_{inh} , which shows that shell covering inhibits nutrient elution from sediment. The variables IR_N , IR_P were calculated with the data of the shell-covered sediment experiment in the next chapter. The time series of Φ_{inh} were set up as imaginary patterns (Fig.5).

$$(1 - \Phi_{inhN}) \frac{IR_N}{Z} \theta_N^{T-20} \quad (5)$$

$$(1 - \Phi_{inhP}) \frac{IR_P}{Z} \theta_P^{T-20} \quad (6)$$

2.1.4 Design for numerical experiment patterns

Table 1 indicates the various ways to reduce external load and internal load in the main drainage canal. The experimental patterns listed in Table 2 were generated by combining these ways, and

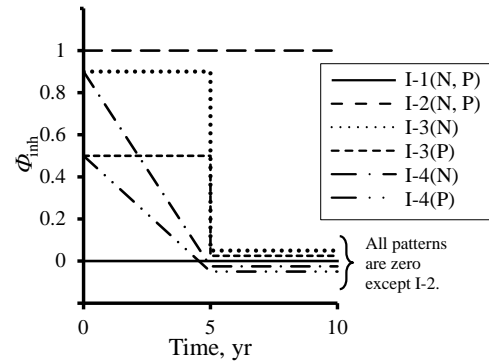


Fig. 5 Inhibition patterns on internal load from sediment

numerical experiments were carried out.

Three ways of reducing external load are shown in Table 1, and the contents are as follows. The symbols are E-1 for reducing external load by 0%, E-2 for reduction by 25%, and E-3 for reduction by 50%. Reduction by 0% means no remediation measure. Preliminary numerical experiments resulted in deciding reduction values such as 25% and 50%. While the reduction values are not based on any theory, the author will ensure that the external load is reduced by 25% or 50%. It was expressed in the calculation for the reduction of external load that the concentrations of all effluents like rainfall runoff were equally decreased.

Four kinds of ways to inhibit nutrient elution are shown as remediation measures against internal load in Table 1. Inhibition ratio Φ_{inh} here means how much oyster-shell covering inhibits nutrient elution from sediment compared with non-covered sediment. No remedy, shown by I-1, means that Φ_{inh} is zero. Perfect dredging of I-2 was supposed that all sediment was clear off in canal bottom, then Φ_{inh} was 100%. The patterns of covering types 1 and 2, shown by I-3 and I-4, both mean that the sediment was covered with oyster shells. Both patterns were different in the variation of Φ_{inh} . The inhabitation ratio Φ_{inh} s of covering type 1 decreased in a stepwise fashion, and those of covering type 2 decreased linearly. These patterns reflected the elution properties of the shell-covered sediment experiment.

Computational time was decided looking at the previous studies observed at freshwater areas. It was reported that when an irrigation pond was dredged up in Chiba Prefecture, Japan, the dredging effect keeping the chlorophyll-a concentration lower, had been continued for three to four years [14]. Normal sands were used at Lake Kasumigaura for sand covering. The covering effect had been continued for two to five years [10]. Based on the studies, the computational time of inhibition by dredging and shell covering was set up to five years. After that, the dredging effect (I-2) continued for more five years and two type (I-3, I-4) of shell covering disappeared to check the concentration under no inhibition for five years (Fig.5).

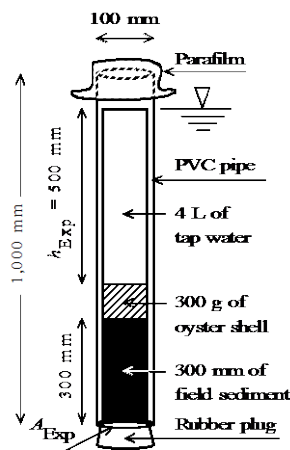


Fig. 6 Experimental arrangements for shell-covered sediment experiment

2.2 Material and methods for shell-covered sediment experiment

2.2.1 Oyster shells for experimental material

Barnacles and muddy blobs were adequately washed out of oyster shells by using a lot of fresh water. Long immersion in fresh water eliminated the salt content in the shells, and the shells were then dried in the sun. Three types of shell sample sizes were arranged for the experiment. The samples were called “original size”, “chip size”, and “powder size”. Chip size samples were kept on a sieve with a mesh size of 4.5 mm after granulating the dried original shells with a hammer. The powder size samples were fine shells passed through the sieve. The shell samples were heated at various high temperatures for six hours in an electric furnace. From a study on the removal of various ions using heated oyster shells, reference [15] confirmed the optimum heated temperature to be 600°C. Therefore, the shells for experiment were heated at four calcination temperatures, 100°C, 200°C, 400°C, and 600°C, except for non-heated oyster shells kept at room temperature. Shell-covered sediment experiments were carried out. The water used for measurement was sampled at the upper part of a pipe used in the experiments. Water samples were subject to an absorptiometer to determine the concentrations of total nitrogen (TN) and total phosphorus (TP).

The surface sediment was sampled at the field. The disturbed sediment sample and pure tap water were set up to make elusive condition from sediment and make the severe condition for shell covering.

2.2.2 Experimental procedure

For the experiments, lumps of sediment 300 mm high were placed into the bottom of a clear PVC pipe, and the air in the sediment was let out (Fig.6).

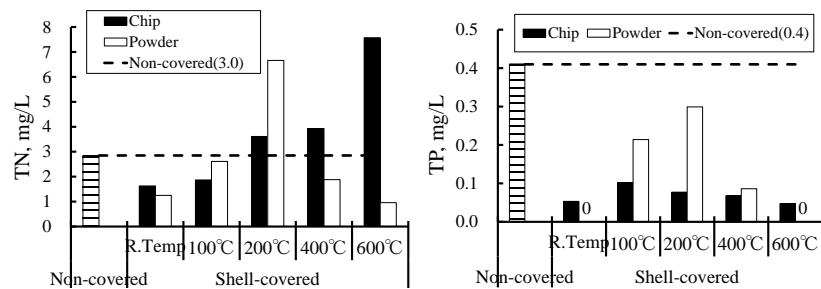


Fig. 7 Result of shell-covered sediment experiment after 10 days (Dashed lines show each concentration under the non-covered)

Sediment sampled at the main drainage canal in K. Town was used. Three hundred grams of shells were put over the sediment, and 4 L of tap water was funnelled with as little erosivity as possible. The upper water in the pipe was periodically sampled, non-filtered, and measured for a period of up to ten days. The shells used were the chip and powder types and were heated at all calcination temperatures. The following experimental processes were not carried out. We did not beat the water in a pipe to make it homogeneous, and we did not control the quality of the water associated with the elution of nutrients such as dissolved oxygen. Elution of nutrients from sediment was supposed to be maximum with tap water containing no nutrients. To make sure there was no phytoplankton growth from the sediment, the experiments were conducted in a darkened room.

The experiments were carried out at the longest for 10 days, and not long term such as for months or years. According to elution tests worked out using many sediment samples from different irrigation ponds in Japan, elution concentrations such as of nitrogen and phosphorus indicated that concentration peak within 10 days or so [16]. If long-term experiments were carried out, it would be necessary to discuss that the nutrients eluted from sediment may change or settle in water in addition to the elution. Ten days is enough for discussing elution from sediment.

3. RESULTS AND DISCUSSION

3.1 Results of shell-covered sediment experiments

3.1.1 Results under non-shell-covered condition

Figure 7 shows the water quality of the water column after ten days for the shell-covered sediment experiments. Under non-shell-covered condition, elution amounts were different in nitrogen and phosphorus. Thus, total nitrogen TN_{10} was 3 mg/L, and total phosphorus TP_{10} was 0.4 mg/L after 10 days.

3.1.2 Results under shell-covered condition

As shown in Fig. 7, both the chip and powder samples had a similar tendency of nutrient elution from the sediments except for the chip sample heated at a temperature of 600°C on TN. While the inhabitation ability of the shell covering diminished in the range from room temperature to 200°C, shells heated over 200°C inhibited the elution from the sediment. The concentrations of nitrogen and phosphorus with no heated shells was as low as those with shells heated in a high temperature range of 400 - 600°C, except for TN at 600°C in the experiments. Therefore, pre-treatment such as graining and heating might be in vain, and non-heated shells at both sizes will be optimum.

Inhibition ratio of nutrient elution was different in water quality items such nitrogen and phosphorus. First, the TN concentrations with chip and powder samples at room temperature were determined to be 1.63 mg/L and 1.25 mg/L, respectively. Therefore, shell covering inhibited elution by 50% compared with the non-shell-covered condition. Second, the TP concentrations of the chip and powder were 0.05 mg/L and 0.00 mg/L, respectively. These differences mean that the shell covering inhibited elution by 90% compared with the non-shell-covered condition.

3.2 Parameters for model nutrient elution from sediment

The variables of IR_N and IR_P used in Eq. (5) and (6) were calculated like Eq. (7) and (8) by using parameters under the non-shell-covered condition. According to the specifications of apparatus used in the experiment and experimental conditions, water column h_{Exp} was 0.5 m long, as shown in Fig.6, and experiment time D_u was 10 days as mentioned above. For the non-shell-covered condition, the concentrations of TN_{10} and TP_{10} were 3 mg/L and 0.4 mg/L, respectively. The values of IR_N and IR_P , assessed at 0.15 and 0.02 g/m²/d, respectively, were in good agreement with those of Lake Suwa [17].

$$IR_N = \frac{TN_{10} \cdot A_{Exp} \cdot h_{Exp}}{A_{Exp} \cdot D_u} = \frac{3 \times 0.5}{10} = 0.15 \text{ (g/m}^2\text{/d)} \quad (7)$$

$$IR_P = \frac{TP_{10} \cdot A_{Exp} \cdot h_{Exp}}{A_{Exp} \cdot D_u} = \frac{0.4 \times 0.5}{10} = 0.02 \text{ (g/m}^2\text{/d)} \quad (8)$$

Two things were simplified in the paper. First, elution test as non-shell covered sediment experiment under various water temperatures was not carried out for elution model equation. Though the IR_N and IR_P were obtained under one temperature condition, these values were in good agreement with those of a Japanese lake. Thus, the third terms of Eq. (3) and (4) were corrected by using each one experimental data of nitrogen and

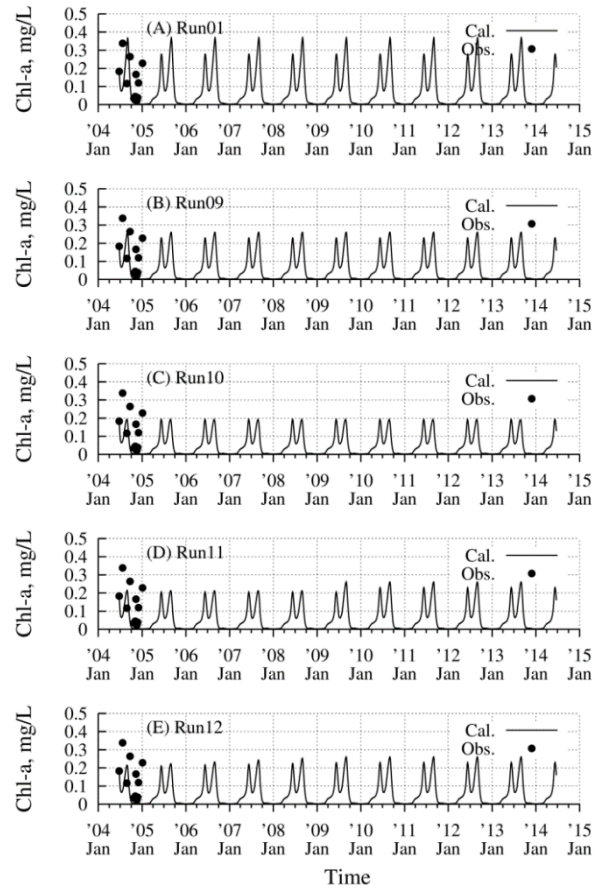


Fig. 8 Several results of numerical experiments

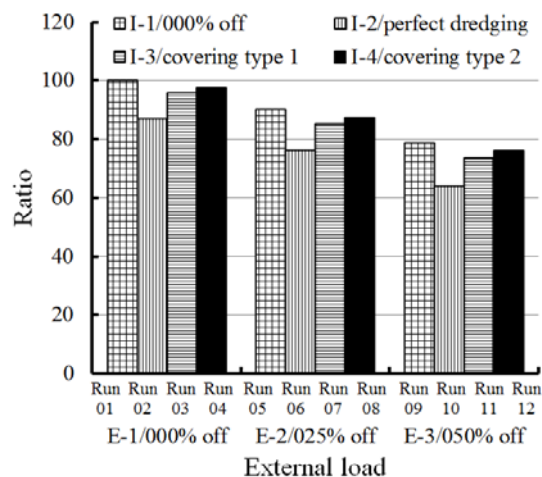


Fig. 9 Comparison of integrated concentration of chlorophyll-a during 10 years shown in Fig.8

phosphorus, respectively. Second, not the undisturbed sediment samples but disturbed samples were applied to elution tests. Oyster-shell covering condition might be severe as elution condition in the respect of using disturbed samples in addition to use tap water not field water. It was again noticed that the values of IR_N and IR_P obtained under this experimental condition were in the proper range of a Japanese lake.

3.3 Results of numerical experiment

Figure 8 introduced several simulation results on the concentration of chlorophyll-a. For Run01, there was no remediation measure against both external and internal loads. While Run09, Run10, Run11, and Run12 were in common reduction series of external load by 50%, these series were different in terms of remediation measure against internal load. For Run09, there was no remedy, I-1, against internal load. For Run10, there was perfect dredging against internal load, I-2. Run11 and Run12 for covered sediment mean covering type 1, I-3, and covering type 2, I-4.

The chlorophyll-a concentrations of Run10, Run11, and Run12 under the reduction of internal load demonstrated the same that of Run09 in 10 years except for Run10. If the bottom sediment is ideally dredged and sustained to be dredged, then a concentration of chlorophyll-a like that of Run10 might be kept much lower than the others. While the concentration of chlorophyll-a for covering type 1 like Run11 was inhibited the same as that by the dredging of Run10 for the first half of ten years, the latter concentration of chlorophyll-a was the same level as that of Run09, which had no remedy.

The concentration of chlorophyll-a for covering type 2 such as Run12 gradually became the same as that of Run09 with no remedy over 10 years. Figure 8 presented a 50% reduction of the external load mentioned above, except for Run01. The results for a reduction of 25% had similar tendency. As you can see, only a simple interaction was shown, and simulation is different from the actual world. For example, it is very difficult to keep the perfect dredging condition.

3.4 Estimation of remediation measure

To evaluate various remediation measures, the concentration $A(t)$ of chlorophyll-a was integrated over the 10 years. The integration result is shown in Fig. 9, in which each integration results is recalculated with a value of 100 representing the integration of Run01's $A(t)$.

It was predictable that perfect dredging would have the best effect for the various remediation measures against internal load. Comparing Run02 with Run05, it was better to dredge than to reduce external load somewhat. The reduction of external load was also needed to sustain the inhabitation effect of dredging.

Only shell covering might have a small effect on water quality improvement. Good water quality is expected to be achieved through a combination of reducing external load and this shell covering. The water quality problem cannot be corrected in a short time, so it is a problem that should be continued to be tackled over a long period of time. One approach

would be to use various kinds of bioresources, and prolonged activity is needed to do. In the author's experience, application to the field is often quite tough. It was tried that aquatic plants were grown in style of floating island, and nutrient in water was imbibed by the plants in the pursuit of clear water in the main drainage canal. Many turtles eat up aquatic plant rootage growing out of floating island, which results in aquatic plants not growing.

If concentrations at various times instead of concentration integration were used for judgement, then it would be convenient to compare the concentrations with water quality standards. In this paper, the concentration above was not selected, because a complex simulation model or enough input data was not required for calculation. Integration of concentration over 10 years would cover the various shortages of the simulation.

4. CONCLUSION

An oystershell-covered sediment experiment was carried out, and the properties of nutrient elution from sediment and experimental parameters were obtained. The shell-covered sediment model, which reflects the experimental parameters of elution, was added to the ecosystem model. A numerical experiment was investigated on reducing patterns against external load and internal load to evaluate the various remediation measures.

Sample graining such as chip and powder and various heated temperatures were investigated in the experiment. Pre-treatment such as graining and heating might be in vain, and non-heated shells of chip or powder size are optimum.

Under non-shell covered condition, TN and TP concentrations for 10 days were determined, and IR_N and IR_P were 0.15 g/m²/d and 0.02 g/m²/d, respectively. These values of IR_N and IR_P were used as parameters of the numerical model.

Experiments under the non-shell covered condition resulted in elution nutrients such as nitrogen and phosphorus being different in inhibition ratio. First, for the nitrogen concentration of the chip and powder samples, shell covering inhibited elution by 50% compared with the non-covering condition. Second, the covering on phosphorus inhibited elution by 90% compared with non-covering.

Twelve reducing patterns in the combine of external load and internal load were investigated in a numerical experiment. The ways of reducing external load consisted of no remedy, reduction by 25%, and reduction by 50%. The remediation measures of internal load had four kinds: no remedy, dredging, covering type 1, and covering type 2. The inhibition ratio of covering type 1 followed a stepwise decrease. The ratio of covering type 2 decreased linearly. The concentration of chlorophyll-a was integrated over 10 years to

evaluate various remediation measures.

It was predictable that perfect dredging would have the best effect on various remediation measures against internal load. If dredging work is properly accomplished, then its performance will have a profound effect on water quality improvement. Only shell covering might have a small effect on water quality improvement. Good water quality is expected to be archived through a combination of reducing external load and this shell covering. While bioresources such as water plant is planned to be promoted, other living things and conditions could disturb the system.

5. ACKNOWLEDGEMENTS

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