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A Possible Scenario for Environmental Remediation in Coastal Waters by Use of Phytoplankton and Waste Materials

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Summary

Eutrophication followed by a decline in biodiversity has become prominent in the coastal marine environment around Japan. We must pursue a way to remediate the environment without a reduction of seafood production. Since environmental remediation and food production should be long-term programs, we must perform this inexpensively, avoiding the consumption of extra energy and resources. One practical way is the reuse of waste materials. Steelmaking slag is a massive waste containing some essential elements for phytoplankton growth such as iron, phosphorus and silicon, which are usually short in supply in the eutrophied coastal waters which have arisen from the discharge of urban sewage containing very high levels of ammonium. We have done several enrichment experiments with the slag in land and shipboard laboratories to determine the availability of the elements originating from the slag. Some experiments were also done with sewage to test the combined effects of both wastes on phytoplankton growth. Based on the results obtained, we stress the practical value of such enrichments to achieve the remediation of the environment and the food production simultaneously.

Key words: environmental remediation, phytoplankton, seafood production, sewage, steelmaking slag

Introduction

Japan, and most industrialized countries as well, emit CO_2 by consuming fossil fuel and discharge urban sewage by consuming foodstuffs, which cause global warming and eutrophication of coastal waters, respectively. Among them the latter is a major cause of the decline of biodiversity in the coastal environment. Heavy industries also discard huge amounts of waste materials, which cause further environmental deterioration. For example, at present Japan emits 4.9% of world's CO_2 emission (*fide* Environment Agency of Japan, 2000). Japan imports ca. 50 x10^6 metric tonnes of food, and feed and harvests nearly 10 x10^6 metric tonnes of fish every year. These, along with 2 x10^6 metric tonnes of newly produced nitrogenous fertilizers, are the main source of the annual addition of nitrogenous nutrients into Japanese coastal waters. Therefore, the amount of 'new' nitrogen is estimated to be approximately 3.6 x10^6 metric tonnes per year. In addition, Japan imports 250x10^6 kl of crude oil that contains 0.05-0.4% nitrogen and Japan has an annual precipitation of 680x10^{12} l that contains allochthonous nitrogen at an average concentration of 1.4 mg/l.

On the other hand, owing to use of phosphorus-free detergents since late 1970s, the input of new phosphate in the coastal waters has greatly decreased. This has resulted in hypernitrogenous or phosphorus limiting condition of Japanese coastal waters. In some heavily eutrophied areas like Osaka Bay located in the Inland Sea of Japan, silicate has also become limiting in relation to the Redfield ratio, despite the continual input of riverine silicate originating from soils rich in volcanic ash. Such an unbalanced composition of nutrients due to anthropogenic loading is responsible for frequent occurrences of nuisance algal blooms (*e.g.* red tides) in the last two decades, surpassing the healthy growth of natural phytoplankton communities, which are usually dominated by diatoms.

Steel manufacturing produces around 250 kg of residue, or steelmaking slag, for every ton of steel produced. The slag production has reached nearly 25x10^6 metric tonnes per year in Japan. While the majority is used for reclamation, a significant portion has been disposed of as waste in landfill areas. The steelmaking slag contains some elements essential for the healthy growth of phytoplankton, such as iron, phosphorus and silicon, and its growth potential has recently been confirmed for marine diatoms and other phytoplankters (Nakamura *et al.*, 1998, 1999). Therefore, by introducing phosphorus, silicon and iron originating from the slag into the hypernitrogenous coastal waters, the coastal waters can be turned into eutrophic waters, where desirable phytoplankton, and seaweeds as well, can grow with a balanced nutrient availability.

To test this idea, we carried out several experiments to determine the effect of the slag with or without sewage on the growth of cultured strains of various phytoplankters and natural assemblages of mixed phytoplankton in laboratories on land and at sea. In this paper, we describe the scenario rather than the results obtained by these experiments, which are given elsewhere (*cf.* references cited).

Materials and Methods

In the first series of the experiments, we cultured a natural phytoplankton assemblage in filtered coastal seawater enriched with treated sewage at different concentrations. The sewage was obtained from the final treatment pools of the Sendai Municipal Sewage Treatment Plant at an exhaust pipe leading to the neighboring Sendai Bay (Haraguchi, 1997). It contained rich inorganic compounds, but free from organic substances as well as toxic heavy metals. Its quality is continually monitored and adjusted by the treatment plant.

In the second series of the experiments, we determined availability of the elements released into water from steelmaking slag for several monospecifically cultured phytoplankters in the laboratory (Nakamura *et al.*, 1998 ; Arita *et al.*, 2003a, Haraguchi *et al.*, 2003) and of natural phytoplankton assemblages in large-volume outdoor tanks on shore (Nakamura *et al.*, 2003 ; Nakamura and Taniguchi, 2003). Similar experiments were also done in a shipboard laboratory (Nakamura *et al.*, 1999 ; Haraguchi, 2001). In the third series of the experiments, the combined effect of the sewage and slag on the growth of a cultured phytoplankter (Arita *et al.*, 2003b) and natural phytoplankton assemblages (Haraguchi and Taniguchi, 2003) was determined in our laboratory. The same experiments were carried out on board ship in the subtropical and transition waters in the western North Pacific (Haraguchi, 2001). The subtropical water is severely oligotrophic, while the transition water is comparatively eutrophic.

The slag used in these experiments was classified into dephosphorization slag, desiliconization slag and decaburization slag, depending on the steelmaking processes and therefore the resulting elemental composition is variable. The basic component of slag is CaO, which can inhibit phytoplankton growth by increasing the pH of the medium when added in high concentrations. Various compounds exist at various concentrations, some of which are known to be effective elements for phytoplankton growth such as iron, silicon, phosphorus, etc. It must be noted, however, that the slag contains very few toxic heavy metals (Tables 1 and 2).

In all the experiments, we compared the growth of phytoplankton in the enriched treatments to that in the non-enriched treatments by determining the concentrations of chlorophyll *a* and phytoplankton cell numbers. The change in

Table 1. Percent composition of chemical compounds in steelmaking slag

Element	%	Element	%
Total Fe	20.1	SiO_2	8.56
FeO	16.35	P_2O_5	2.27
Fe_2O_3	7.63	MnO	3.5
Metallic Fe	2.12	Total S	0.021
Total CaO	50.07	MgO	7.25
Free CaO	18.21	Al_2O_3	0.41
CaF_2	1.07	Na_2O	5.8

Table 2. Concentration of major elements in saturated solution of steelmaking slag in distilled water ($\mu g/kg$)

Element	μg/kg	Element	μg/kg
P	90-110	Al	4.2-12
Fe	10-30	Co	0.7-1.6
Mn	31-32	Zn	<5.4
Si	3.31-4.88 ($\text{x}10_3$)	Ni	<2.2
Mg	1.85-6.11 ($\text{x}10^5$)	Cu	<2.1
Ca	38.5-44.1 ($\text{x}10^5$)	Cr	<0.5
Ba	200-215	Cd	Not detected

species composition was also determined, when the natural assemblage was cultured.

Results

Growth enhancement by sewage

Since the urban sewage used was extremely hypernitrogenous, containing ammonium ions at very high concentration (>1.5 mM), the culture medium enriched with the sewage was very rich in nitrogen, slightly poor in silicate but severely phosphate-limited. Nevertheless, the growth of the natural phytoplankton assemblage was prominent in the medium. When the medium was enriched further with phosphate, the final yield was naturally the highest. Yields of diatoms and other phytoplankton were equivalent, while the species composition of the diatoms was altered. Among the diatoms, *Thalassiosira* spp. replaced *Skeletonema costatum* as the dominant species (Haraguchi, 1997). In later experiments, however, the additional enrichment of a slag altered the assemblage and diatoms dominated due to this fast growth (Haraguchi and Taniguchi, 2003). This means that the enrichment not only increased the final yield of the phytoplankton assemblage but altered the species composition of the assemblage.

An interesting result was that no marked decline in growth and yield was observed even at higher concentrations of ammonium reaching 610 μM (Haraguchi, 1997), which exceeded the reported inhibiting concentration for diatom growth (ca. 250 μM) (Matsue, 1984). Ammonium toxity is dependent on pH ; the toxity increases with increasing pH. The latter value was derived from the culture experiments made in a medium enriched with ammonium. This indicates that the inhibition by excess ammonium can partly be mitigated by the buffer action of the water enriched with sewage, which contains various ions.

Growth enhancement by steelmaking slag

Growth rate and final yield of all species tested were more or less enhanced by the enrichment with the slag solution. The degree of the growth enhancement and responses to the enrichment of different concentrations were different with different species. For example, such species as *Thalassiosira angulata* and *Amphidinium carterae* attained the highest yield at the highest enrichment. On the other hand, although the yields of *Chaetoceros gracile*, *Rhodomonas lens* and *Emiliania huxleyi* were larger under lower enrichment, their growth was inhibited by higher enrichments (Nakamura *et al.*, 1998). Similarly, a shift in the size spectrum of phytoplankton chlorophyll *a* to a larger size fraction due to enrichment of the slag solution was also recorded at sea (Nakamura *et al.*, 1999). However, in the severely oligotrophic surface waters that contain little nitrogenous nutrients, slag enrichment alone could not enhance the growth of phytoplankton (Nakamura *et al.*, 1999 ; Haraguchi, 2001).

This was confirmed in laboratory experiments that iron, phosphorus and silicon released from a slag are actually effective as the essential elements for phytoplankton growth. Obvious growth enhancement was recorded in the medium supplied with these elements originating from the slag, instead of reagent chemicals usually used for standard culture media (Arita *et al.*, 2003a).

On the other hand, excess enrichment of the slag (*e.g.* over 3300 mg/l) inhibited growth of phytoplankton severely, mostly because of increased pH that sometime exceeded 10 (Haraguchi *et al.*, 2003). The pH is determinative in the inter-speciation of inorganic carbon. As pH increases, CO_2 aq. shifts toward HCO_3^- and CO_3^{2-}, which are less available for marine phytoplankton. No species attained their maximum growth rate when the pH was over 9 and most species could not grow at around pH 10 (Haraguchi *et al.*, 2003 ; and *cf.* Hansen, 2002). These results indicates there exists an optimal concentration of slag enrichment as a nutrient source for phytoplankton. A low dose of the slag which also avoids an increase in pH is recommended in the case of enrichment in field. Since the effective dose may be variable with kind of slag, the dose should be determined for each kind of slag used.

Combined effects of simultaneous enrichment with sewage and steelmaking slag

Growth of cultured phytoplankters and natural phytoplankton populations was almost always enhanced by the simultaneous enrichment of sewage and steelmaking slag (Haraguchi, 2001 ; Arita *et al.*, 2003b ; Haraguchi and Taniguchi, 2003). The degree of the growth enhancement was exceedingly high, as was expected, in the oligotrophic subtropical Pacific waters (Haraguchi, 2001). In these experiments, it was observed that the enrichment was selectively effective for diatoms and consequently it increased the average cell size of the natural assemblages (Haraguchi, 2001 ; Haraguchi and Taniguchi, 2003).

On the other hand, excessive enrichment with 200 mg/l of slag and 40% sewage suppressed phytoplankton growth, while no suppression of the growth was recorded with 40% sewage alone. The suppression with 200 mg/l of slag became severe as the concentration of the sewage increased. An increase in the pH due to excess enrichment of the slag, shifts equilibrium between NH_3 and NH_4^+ toward NH_3, which is strongly toxic. Therefore, slag enrichment is most effective at a lower dose to avoid an increase in pH. Although simultaneous enrichment with 20 mg/l of slag and 20% sewage was confirmed to be the best dose at 10°C, the dose should be reduced during the summer since the ratio of NH_3 to NH_4^+ increases with increasing temperature. The increase in pH also inhibited the phytoplankton growth in another way, by inhibiting the release of available phosphorus from the slag into the medium (Haraguchi and Taniguchi, 2003).

Discussion

Background of the scenario

Global environmental deterioration and food shortages will likely be the most difficult problems that humankind must overcome in the 21st century. One of the most serious and difficult environmental issues is the increase in atmospheric CO_2. Several technical methods have been proposed to remove CO_2 from the atmosphere in the field of engineering. However, such technical aids are, though immediately and highly potent, basically temporary measures that often causes another problems. For example, although dumping of liquefied or frozen CO_2 into the deep sea seems to be a direct and immediately effective solution, it may actually be hazardous for the deep-sea ecosystems (Seibel and Walsh, 2001). To avoid such uncertain technologies, we must pursue more reliable solutions with the least risk of producing other problems. Employment of biological activities is likely an ideal solution. But it must be carried out on large spatial and longer temporal scales to be effective in a global sense, because biological processes usually work slowly. In other words, reliable global environmental remediation is a costly project that should be persistently continued. If the remediation project produces other valuable products simultaneously, the cost of the achievement would be improved. Hence, good remediation projects must be multi-purpose.

Japanese case

Current eutrophication of coastal waters in Japan and other countries is caused by excess loading of unbalanced nutrients and the modification of the coastal ecosystems into simplified systems, as seen in red tide phenomena. However, since such unbalanced eutrophication is caused by loading with hypernitrogenous sewage, the nutrient composition of the seawater can be balanced by

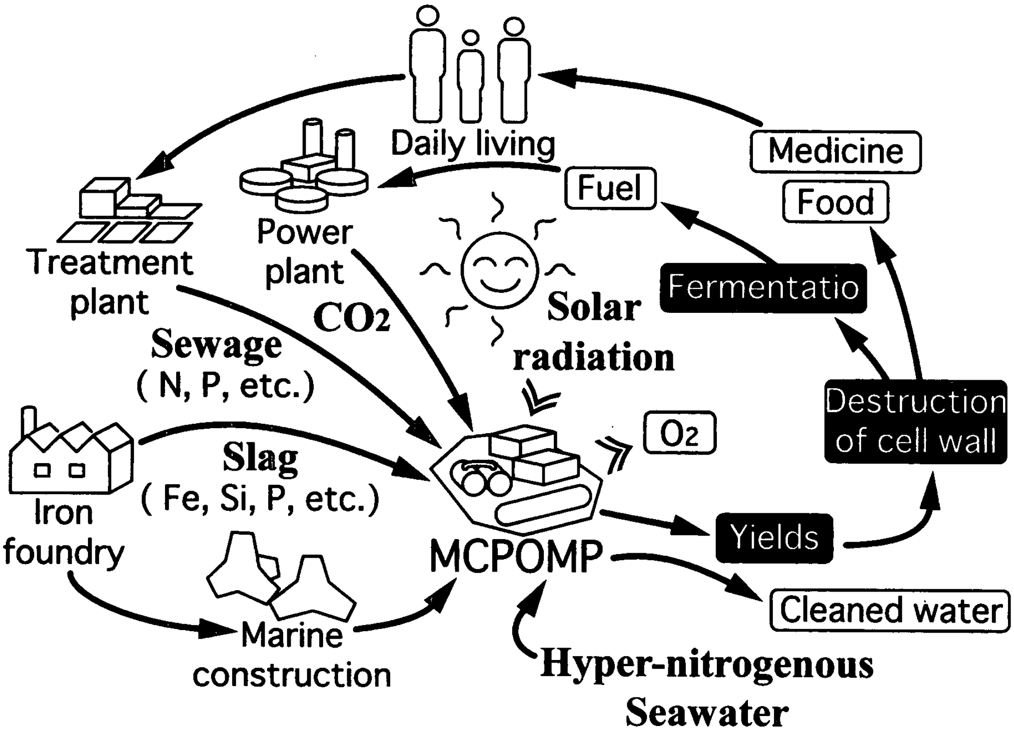

FIG. 1. A conceptual presentation of marine environmental remediation in coastal areas by use of phytoplankton. A mass culture plant of marine plants (MCPOMP) reuses waste materials such as urban sewage, steelmaking slag and CO_2 as resources for building organic materials. The organic matter produced by phytoplankton contains some physiologically effective substances and can be used as food and feed or offered to fuel fermentation. The water containing less nitrogenous nutrients is finally discharged from the MCPOMP and this water may suppress nuisance algal blooms in a coastal area. Steelmaking slag may also be used as the port and harbor construction materials, which would be functional in converting hypernitrogenous neritic waters in semi-enclosed areas into balanced eutrophic waters.

the additional enrichment of phosphate, silicate, iron, etc. It would be less expensive, if we obtain these elements from other waste materials like steelmaking slag. Once elemental composition of the nutrients can be balanced (*e.g.* Redfield ratio of $N : P : Si = 16 : 1 : 15$), eutrophy will likely produce a diversified, stable, balanced ecosystem that fixes more CO_2 into organic matter. The produced organic matter can be used in various ways; foodstuff and materials for new products such as medicine and diet food or feed for cattle and cultured fish. In other words, it can be a multi-functional enterprise, simultaneously reutilizing waste materials including CO_2, producing food, feed and new products, and remediating the hypernitrogenous marine environment as well. This is a practical idea, particularly in Japan, because for most of the populated towns and cities, their sewage treatment plants and developed industrial yards are concentrated into the coastal areas (Fig. 1).

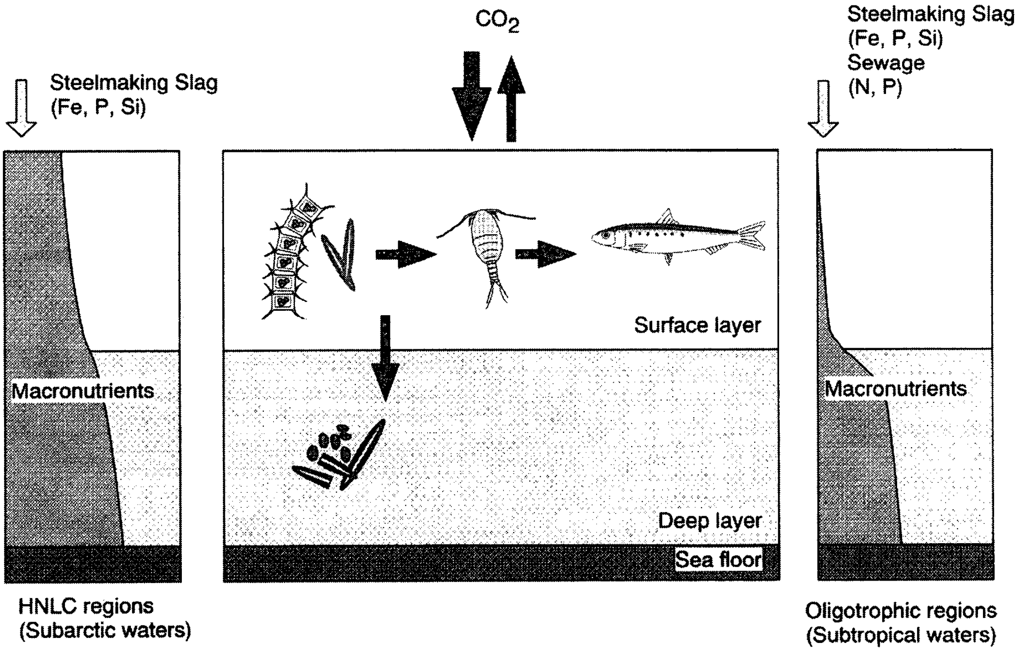

FIG. 2. A possible application of the scenario of marine environmental remediation by use of phytoplankton to open ocean. While a sole enrichment with steelmaking slag is workable in the HNLC (high nitrate low chlorophyll) areas, mixed enrichment with the slag and sewage is needed in the oligotrophic area. Part of organic carbon produced is respired in the surface layer and the other part is transferred to fisheries resources or sent to depths in the ocean.

To apply this scenario, however, wise and appropriate precaution must be paid to remove toxic substances such as carcinogens and heavy metals from the sewage and slag. During the 1950s and 1960s, Japan suffered from tragic pollution-induced diseases, such as Minamata Disease caused by organic mercury and Ache-ache Disease caused by cadmium. In both cases, pollutants were ingested by the victims via seafood that absorbed and accumulated the pollutants from coastal waters. Other organic and inorganic pollutants were also found from several natural water bodies. After these cases, numbers of the laws relating to conservation of water quality and the environment were enacted in the 1970s. These laws require every kind of government undertaking and organization, as well as the cooperation of agricultural and livestock farmers who discharge sizable amounts of wastewater, to remove all pollutants before discharge. Although the acceptable concentration is basically 10 times that of drinking water, the actual concentration of the pollutant is usually lower than the detection limit of current analytical methods. The number of the target pollutants usually reaches 40, including various organic compounds originating from pesticides and solvents, heavy metals from catalysts, inorganic nitrogenous and phosphoric compounds, coliform bacteria, etc. In addition to these, turbidity, suspended matter and its organic content, chloride ions, surfactants, pH, dissolved oxygen, and temperature are also checked.

An important fact in Japan is that these laws are being intensified by penal regulations, under which local governments frequently and strictly inspect if these pollutants leak into sewage from factories, farms and other institutions. Such organizations, therefore, invest a large amount of money to keep their sewage pollutant-free. For example, our Tohoku University holding about 10,000 students invests *ca.* US$ 300,000 every year just for monitoring the pollutants in the discharged waters, besides the enormous cost to remove pollutants from the waters. Although the waters from private houses and home manufactures are not inspected, they are treated in the municipal treatment plants. The city of Sendai, with a million people, spends *ca.* US$ 5,000,000 a year to operate three sewage treatment plants. As a result, fairly clean sewage is discharged into the coastal seas, where various sea foods are regularly harvested and consumed by Japanese people who enjoy the world's longest longevity.

Conclusions

It is often said that expansion of food production is essentially contradictory to conservation of the natural environment/ecosystems. However, we would like to stress that it is the case in agriculture on land, but not always true for the marine ecosystems. High biological productivity can be maintained in the marine environment without an excess simplification of the natural ecosystems, which makes the ecosystems vulnerable (*cf.* Taniguchi, 1996, 2001). Therefore, the present scenario to restore the ecosystems and to produce seafood in the coastal marine environment by enhancing phytoplankton production by enriching with sewage and slag can be one of the most reliable alternatives in the future.

On the other hand, we must pay attention to ecological consequences of the enrichment. Our results indicate that the effect of the enrichment is more or less selective. Therefore, since the enrichment would modify taxonomic composition of the phytoplankton assemblages, we must avoid the possible oversimplification of the natural assemblages. Our results, at the same time, demonstrate that such enrichment is generally more effective on diatoms, which usually link to the so-called grazing food chain up to fish. This means that the amount and ratio of the sewage and the slag to be employed can regulate the structure of the assemblages.

Enrichment of iron, silicon and phosphorus originating from the slag may also be applicable in the so-called high nitrate low chlorophyll (HNLC) areas (Martin *et al.*, 1990 ; Harrison *et al.*, 1999), while the phytoplankton assemblage must be altered to a diatom dominating one. The combined use of the slag and sewage is theoretically possible to enrich even the vast oligotrophic open ocean. Growth enhancement of only a few % can absorb significant amounts of atmospheric CO_2 over vast areas. It is important to note that these enrichments should be a good security to avoid uncertain technologies such as ocean dumping of CO_2, which would give rise to other problems.

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