1. Introduction

Apart from very wide countries and inland countries, significant part of the world population is concentrated into marine coastal areas. Human activities there have been dramatically increasing flux of agriculture runoff and sewage containing ammonium, nitrate and phosphate, which act as macro-nutrients of phytoplankton in the coastal waters and cause an over proliferation of the phytoplankton or red tide phenomena. Among such inorganic elements, phosphate has recently been cut-down by regulating production/consumption of phosphate-based detergents so that the marine coastal environments turn to hyper-nitrogenous and phosphate limiting conditions. Under hyper-nitrogenous condition, so-called harmful algae, which can vitally grow on a wide variety of alternative phosphorous compounds other than phosphate, appear to dominate and often bloom extensively.

A harmful algal bloom would hardly break out when prevailing competitors coexist. Diatoms are the most probable competitors, because their growth rate usually exceeds one division a day, while most harmful algae grow at a rate of one division a day at most. Since growth of the diatoms is enhanced under balanced supply of phosphate and silicates with nitrate/ammonia, additional enrichment of phosphate and/or silicates is required to turn the hyper-nitrogenous environments into healthy ones. Growing healthy diatoms are easily linked to grazing food chain so that such an enrichment would be an effective way to work a nitrogen cycle regularly in the coastal environments. The food chain which can be established would be analogous to that in the upwelling systems, where significant part of the global marine fish catch is harvested every year.

Sources of phosphate and silicate to be enriched are in question. Since huge amount of the resources are required to balance the entire hyper-nitrogenous coastal waters, it should not be synthetic fertilizers which are produced by use of much energy consuming fossil fuel. One of the ideal sources is the steelmaking slags, which are a by-product in the iron ore with refining process of steel manufacturing. Main component of the slags is CaO, which prevents reuse of the slags on land due to expansion when react with water. Some 30% of the slags being produced to...
experiments, natural seawater containing a phytoplankton assemblage was incubated with different concentrations of slags to examine an effect of slag concentration on phytoplankton growth. Evaluation of the amount of nutrients including phosphate and silicate released from the slags to seawater was also done. In the second series, we did similar incubations but with a pure culture of the centric diatom *Thalassiosira guillardii* to eliminate effects of grazers on phytoplankton, which usually coexist in the natural phytoplankton assemblages.

2. Materials and Methods

We tested two kinds of steelmaking slags in the following experiments, *i.e.*, decarburization (de-C) and dephosphorous (de-P) slags. Their chemical compositions analyzed by ICP method are given in Table 1, showing higher concentration of phosphorous in the de-P slag. The slags were ground individually into small particles and the smallest fraction of 5–20 μm was sieved out. Fine particles would be expected to release dissolved elements fast and to sink slowly in seawater.

2.1. Experimental Procedure

Exp 1: In the first series of the experiments, the surface seawater including a natural phytoplankton assemblage was incubated, which was collected on 22 October 1998 at Sendai Port, Miyagi Prefecture, Japan facing to the Pacific Ocean. Water temperature was 19.2°C at the collection. The water was filtered through a 330 μm mesh net to eliminate larger grazing zooplankton and brought to laboratory. Fine particles of the de-C slag and the de-P slag were added separately to each of culture vessels containing 30 ml of filtered (330 μm) natural seawater. The vessels were photometric cells (Pyrex) of 25 mm in diameter and 150 mm long for the fluorometer used (Turner Designs Model 10-AU). These cells were acid-cleaned and sterilized before every experiment. The final concentrations of the slags were 0 (control), 0.033, 0.33, 3.3, 33, 330 and 3 300 mg/l and culture made at each concentration was done in triplicate. Apart from the culture experiments, a leaching experiment was also conducted to determine the amount of dissolved nutrients released from the slags into the seawater. The slag particles were added to duplicated autoclaved isopore filtered (0.2 μm pore sized Millipore: Type GTTP) seawater at corresponding concentrations to the preceding culture experiments.

Exp 2: In the second series of the experiments, ESAW medium*1* prepared from an artificial seawater of known chemical composition was used (Table 2),10*. In addition to this, we prepared two kinds of slag solutions, *i.e.*, with or without EDTA, to easily remove bacteria just before use by filtration and to easily dilute to fixed concentration of the dissolved elements. The solutions were prepared by adding de-C slag particles (5–20 μm) at concentration of 330 mg/l to the mixed Solutions I and II shown in Table 2 without or with EDTA (9.8 μM). The slag particles with or without EDTA were suspended by shaking the bottles several times a day for 3 days at 15°C. Then these particles were removed by filtration through an isopore filter (0.2 μm pore size). Each solution was added to the mixed Solutions I and II without or with EDTA at concentrations of 100%, 10%, 1%, 0.1% and 0%, which were equivalent to slag concentrations of 330, 33, 3.3, 0.33 and 0 mg/l made in Exp 1. Furthermore, each diluted solution was added with all

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*1 ESAW is an artificial seawater medium for marine phytoplankton. The original paper compared the growth of 20 strains of diatoms in enriched natural seawater versus ESAW and determined that 19 strains grew equally well in ESAW.

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| Table 1. | Chemical composition in percentage (mass%) of de-C slag and de-P slag used (Hino, private communication). |
|-----------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Fe    | Si     | Ca    | Mn   | Mg   | P    | S    | Al   | Ti   | other elements |
| de-C slag      | 17.9  | 14.1  | 43.4  | 3.4  | 8.6  | 2.1  | 0.1  | 2.8  | 0.9  | 6.9            |
| de-P slag      | 7.3   | 12.7  | 59.1  | 1.4  | 6.8  | 3.4  | 0.6  | 4.5  | 1.4  | 2.8            |

| Table 2. | Formula of ESAW medium (Harrison, 1980). All solutions were sterilized by autoclaving at 121°C for 20 min. except that Enrichment solution Vitamine was sterilized by filtering through a membrane filter of 0.2 μm in pore size. |
|-----------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Solution I      | NaCl   | 20.8  | g/Kg  | Na2SO4 | 3.450 | g/Kg  | KCl   | 0.567 | g/Kg  | Na2CO3 | 0.170 | g/Kg  |
|                 | KBr    | 0.0045| g/Kg  | H2BO3 | 0.0225 | g/Kg  | NaF   | 0.0027 | g/Kg  |         |        |       |
| Solution II     | MgCl2 - 6H2O | 9.37 | g/Kg  | CaCl2 - 2H2O | 3.12 | g/Kg  | SrCl2 - 6H2O | 0.021 | g/Kg  |
| Enrichment solution N | NaNO3 | 549  | μM    |         |        |       |        |        |       |
| Enrichment solution P* | NaH2PO4 - 2H2O | 20.0  | μM    |         |        |       |        |        |       |
| Enrichment solution Si* | Na2SiO3 - 9H2O | 106  | μM    |         |        |       |        |        |       |
| Enrichment solution Fe | FeCl2 - 6H2O | 6.6  | μM    | Na2EDTA - 2H2O | 9.8  | μM    |
| Enrichment solution Metal | MnSO4 - 4H2O | 2.4  | μM    | ZnSO4 - 7H2O | 0.25  | μM    | CoSO4 - 7H2O | 0.057 | μM    |
| Enrichment solution B | H3BO3 | 61  | μM    | Na2MoO4 - 2H2O | 0.52  | μM    | Na2EDTA - 2H2O | 5.1  | μM    |
| Enrichment solution Se | Na2SeO3 | 0.010 | μM    |         |        |       |        |        |       |
| Enrichment solution Vitamine | Thiamine | 0.30 | mM    | Vitamin B12 | 0.0015 | mM    | Biotin | 0.0041 | mM    |

* Concentration of Enrichment solution P and Si was modified.
Enrichment solutions except for P and Fe shown in Table 2. Enrichment solutions P and Fe were separately added as below to produce four media of five different concentrations of slag solutions, i.e., without Enrichment solution P (ex.P), without Enrichment solution Fe (ex.Fe), without both solutions (ex.Fe/P) and full media containing all Enrichment solutions. Among these, since ex.Fe and ex Fe/P medium enriched with the slag solution extracted without EDTA did not contain EDTA, EDTA was added to the concentration of 9.8 μM. Contrary, ex.P medium and full medium as well which were enriched with the slag solution extracted with EDTA contained double dose of EDTA. Every medium enriched with either of two kinds of slag solution at five concentrations was inoculated with the cultured diatom Thalassiosira guillardi.

The diatom Thalassiosira guillardi had been isolated from Sendai Port on 24 March 1999 and kept in standard ESAS medium. For the present experiments, cells were preincubated until reaching to stationary phase in an Fe/P depleted medium. Fe/P starved cells were then inoculated into the experimental vessels in triplicate (Pyrex test tubes) containing 30 ml of medium described above. Although slag concentration was diluted by addition of the Enrichment solutions (up to 0.32 ml) and the inoculated culture (0.4 ml), dilution rate was less than 3% (up to 0.72/30) and was not corrected.

2.3. Conditions of Incubation and Analytical Procedure

Vessels for the culture experiments (Exp 1 and Exp 2) and for phosphate and silicate release test (leaching experiment in Exp 1) were capped with a Milipore wrap and incubated under cool-white fluorescence light of 100 μmol s⁻¹ m⁻² with a 14:10 light:dark regime. Temperature was regulated to be 20°C and 15°C in Exp 1 and Exp 2, respectively. All the vessels were agitated gently but thoroughly four times a day.

In culture experiments, phytoplankton yield was directly determined for each culture vessel (photometric cell) by measuring the in vivo chlorophyll a fluorescence every day with a Turner Designs Model 10-AU fluorometer. Effect of suspended slag particles was corrected by use of the suspension for leaching experiment. Nutrient concentrations in cultures and leaching experiment were analyzed after the maximum yield was attained in the cultures, i.e., on Day 4 for 0.033–33 mg/l treatments and Day 7 for 0 mg/l, 330 mg/l and 3300 mg/l treatments. Residual slag particles were filtered off by a Whatman GF/F filter under gentle vacuum (<100 mm Hg) and filtrate (10 ml) were frozen at −80°C until later nutrient analysis. Concentrations of nitrate-, nitrite- and ammonium-nitrogen, phosphate-phosphorus (P) and reactive silicate (Si) were determined with a Flow Solution spectrophotometer (ALPKEM, model 3.900). Total nitrogen (N) was obtained by summing the concentrations of nitrate, nitrite and ammonium. Similar nutrient analysis was done for each culture on the last day of the culture experiments. pH was measured in leaching experiment every day with a pH meter (HORIBA: F-22). Statistical comparisons were performed using one-way factorial ANOVA and multiple comparison tests (Fisher’s PLSD) at a significance level of p<0.05.

3. Results

3.1. Leaching Experiment (Exp 1)

Natural seawater taken from Sendai Port contained NH₄⁺ of 7.5 μM, NO₃⁻ 2.3, NO₂⁻ 9.0 μM, PO₄³⁻ (P) 2.1 μM and reactive silicate (Si) 56 μM. In order to evaluate nutrient release form the slags, slag particles (0.033–3 300 mg/l) were added to autoclaved filtered seawater. Nutrient concentrations in the filtered seawater without slag (0 mg/l) changed to NH₄⁺ 9.1±0.2 μM, NO₃⁻ 1.8±0.1, NO₂⁻ 9.5±0.1 μM, P 2.2±0.1 μM and Si 98±8 μM (n=2) after 7 d. The reason for increased Si in 0 mg/l was unknown, however, increased Si seems to be attributed to autoclave process, which increases temperature and pH caused by loss of CO₂. Silicic acid readily polymerizes and depolymerizes with change in the temperature and pH. Therefore, concentration of released nutrients mentioned below was corrected by this change.

Concentration of N were not affected by additions of de-C and de-P slags (Fig. 1). However, concentration of P increased respectively to 2.4, 5.1 and 19.5 μM by addition of de-C slag at 3.3, 33 and 330 mg/l, though decreased to 1.7 μM by the highest addition of 3 300 mg/l. Based on these values, amount of P leached was calculated to be 0.03, 0.09 or 0.05 μmol from 1 mg de-C slag when the slag was added at 3.3, 33 or 330 mg/l, respectively. Change in concentration of P was not detected when the slag supplied at 0.033 and 0.33 mg/l. Addition of de-P slag at 0.033–33 mg/l kept concentration of P constant. Higher addition at 330 mg/l and 3300 mg/l decreased P to 0.8 μM and 0.1 μM (Fig. 1).

Concentration of Si also remained constant when de-C slag was added at 0.033–33 mg/l, whereas increased to 224 μM in 330 mg/l treatment (Fig. 1). The highest addition of 3 300 mg/l decreased Si to 67 μM. Any change of Si was not detected by addition of de-P slag except the highest addition of 3 300 mg/l where Si decreased markedly to 22 μM (Fig. 1).

Although pH remained stable when de-C slag and de-P slag were added at 3.3 mg/l or less, higher than 33 mg/l addition increased pH with increasing amounts of slags. The highest addition of both slags at 3 300 mg/l dramatically increased pH to 10.1 after 90 min of the addition (Fig. 2).

3.2. Effect of Slag Enrichment on Phytoplankton Growth (Exp 1)

Growth of natural phytoplankton assemblage was enhanced by slag addition at low concentrations but inhibited by higher additions. In vivo fluorescence (IVF) of chlorophyll a quickly increased on Day 1 and attained its peak by Day 3 in control (0 mg/l) and by lower slag additions (≤33 mg/l) (Fig. 3). At 33 mg/l slags slightly enhanced phytoplankton growth and yielded 20% more phytoplankton than in control and other treatments (Fig. 4) (ANOVA; F(12, 22)=71.8, p<0.05). On the other hand, excess slag addition inhibited the growth. At 330 mg/l a lag phase appeared and level of the maximum IVF was lowered to 64% and 90% of control by de-C and de-P slags, respectively (Fig. 4). None of phytoplankton grew when the slags were added at the highest concentration of 3 300 mg/l (Fig. 4).
Fig. 1. Effect of de-C slag (left column) and de-P slag (right column) enrichments at different concentrations on the nutrient concentration in the filtered seawater. Error bars show the range (n=2). Where error bar is not shown, the range is smaller than the symbol.

Fig. 2. Variations of pH of the filtered seawater at different concentrations of (A) de-C slag and (B) de-P slag. First measurement at 3 300 mg/l was 90 min after addition.

Fig. 3. Variations of relative fluorescence indicating amount of chlorophyll a in cultures of natural phytoplankton assemblage with (A) de-C slag and (B) de-P slag at different concentrations (symbols as in Fig. 2). Error bars are not shown to avoid over-complexity (n=3).
which indicates N limitation comparing to the ratio of phytoplankton requirement (16 : 1 : 15). In control, N concentration fell to 0.5 μM by Day 4 and then N : P : Si ratio changed to 3 : 1 : 11 or N limitation became severe and Si became surplus (Table 3). In all de-C and de-P slag treatments except for 3 300 mg/l, N was always limited and lower than 0.9 μM, while Si was always surplus and higher than 11 μM. P decreased to below 0.1 μM except when de-C slag was enriched at 33 mg/l and more. This indicates that P as well as N was co-limited in the slag enrichments at less than 33 mg/l (Table 3). Although phytoplankton did not increase in 3300 mg/l treatments, concentrations of P and Si decreased as seen in the leaching experiment (Table 3, Fig. 1).

3.3. Utility of P and Fe from Slag (Exp 2)

Extent of P and Si releases from de-C slag was similar in the treatments with and without EDTA. Namely, concentrations of P and Si were 7.2 μM or 5.6 μM and 80 μM or 86 μM, respectively. Also EDTA did not change the maximum IVF except for ex Fe/P medium (Figs. 5(A), 5(E)). Only difference between with and without EDTA was observed in time duration till the maximum IVF (Fig. 5). However, we could not discuss this difference since a number of inoculated cells was not uniform in these experi-

| Treatment | N (mg/l) | NH4 (μM) | NO2 (μM) | NO3 (μM) | Si (μM) | PO4 (μM) |
|-----------|---------|---------|---------|---------|---------|---------|
| control   | 0.5     | 0.2     | 0.1     | 0.2     | 17      | 0.15    |
| de-C slag | 0.033   | 0.6     | 0.4     | 0.2     | 0.1     | 30      |
|           | 0.33    | 0.7     | 0.3     | 0.2     | 0.3     | 15      |
|           | 3.3     | 0.4     | 0.1     | 0.1     | 0.2     | 18      |
|           | 33      | 0.4     | 0.1     | 0.1     | 0.2     | 23      |
|           | 330     | 0.4     | 0.1     | 0.1     | 0.2     | 28     |
|           | 3300    | 16.6    | 4.9     | 2.1     | 0.9     | 1.9     |
| de-P slag | 0.033   | 0.4     | 0.3     | 0.1     | 0.0     | 28      |
|           | 0.33    | 0.4     | 0.1     | 0.1     | 0.2     | 20      |
|           | 3.3     | 0.2     | 0.0     | 0.1     | 0.1     | 11      |
|           | 33      | 0.4     | 0.1     | 0.1     | 0.2     | 20      |
|           | 330     | 0.9     | 0.7     | 0.1     | 0.2     | 92      |
|           | 3300    | 17.9    | 5.4     | 2.4     | 10.1    | 31      | < 0.05 |

Table 3. Nutrient concentrations in culture media where the natural phytoplankton assemblage was cultured with de-C slag and de-P slag at different concentrations.

Fig. 4. Effect of (A) de-C slag and (B) de-P slag enrichment at different concentrations on the maximum fluorescence of the natural phytoplankton assemblage. Error bars show standard deviations (n=3).

Fig. 5. Variations of relative fluorescence of Thalassiosira gil-lardii cultured with different amounts of de-C slag solutions extracted (A–D) with EDTA or (E–H) without EDTA (symbols as in Fig. 2). Full media (D, H) contain all Enrichment solutions shown in Table 2. ex P media (B, F), ex Fe media (C, G) and ex Fe/P (A, E) media were excluded the Enrichment solution of P, Fe and both, respectively. Error bars are not shown to avoid over-complexity (n=3).
ments. In full medium IVF increased exponentially and attained its peak on Day 7 with EDTA and Day 8 without EDTA, while a lag phase appeared at the highest addition of 330 mg/l (Figs. 5(D), 5(H)). In ex P medium, which was not supplied with reagent P, the maximum IVF increased with increasing slag concentrations over 3.3 mg/l but never increased under smaller slag enrichment (Figs. 5(B), 5(F) and 6). In ex Fe/P medium, effect of slag enrichment was lower than in ex P medium under slag enrichment over 33 mg/l, while similar at smaller slag enrichment. In ex Fe medium, no or slightly negative effect was observed (Fig. 6).

4. Discussion

4.1. Effect of Slags on P and Si in Seawater

The present results clearly demonstrate that amount of PO$_4^{3-}$ (P) and reactive Si (Si) released from slags depends on kind and amount of the slags added. However, it is interesting to note that the slags decreased P and Si in seawater under certain conditions. It is well known that adsorption, desorption, precipitation and dissolution of P are influenced by pH, concentration of dissolved P and chemical state of P compounds. Release of P from marine sediment is prevented by adsorption of P onto Fe and precipitation with Ca forming appetite.\(^{14-16}\) Behavior of P in soil is controlled by Al.\(^{17}\) Therefore, presence and physico-chemical state of Ca, Al and Fe in the slags should complicate dissolution and adsorption of P in seawater. Adsorption of P by a converter slag is largest at pH 8, while dissolution of P is largest at pH 6 and exponentially decreased with increasing pH.\(^{18}\) In other experiment, P is released from a converter slag to seawater at pH 7-8, whereas removed from seawater at pH 9 due to precipitation of calcium phosphate.\(^{19}\) It is commonly observed in above experiments that concentration of P in water increases under acidic or neutral condition and decreases under alkaline condition.

In the present study, it was observed that excess addition of de-C and de-P slags at 3 300 mg/l removed P from the filtered natural seawater, while P was released from de-C slag added at 330 mg/l or less. A possible explanation for this result is as follows: pH of the seawater increased by slags added at 330 and 3 300 mg/l to 9.3-9.9 (Fig. 2) and then, especially in 3 300 mg/l treatments, P precipitated as calcium phosphate. The amount of the precipitation in de-P slag treatments exceeded that in de-C slag treatments. This is possibly attributed to higher contents of Ca in the de-P slag (Table 1). Although P content in the de-P slag is larger than de-C slag (Table 1), release of PO$_4^{3-}$ was much higher from the de-C slag (Fig. 1). Amount of PO$_4^{3-}$ released from slags is independent of P content but depends on crystal phase of P in the slags.\(^{20}\) Therefore, selection of slags is very important when a slag is used as a source of the nutrients for phytoplankton.

In general the solubility of amorphous silica increases under alkaline conditions. However, concentration of Si decreased under the highest alkaline condition in the present study, i.e., addition of de-C and de-P slags at 3 300 mg/l.

4.2. Effect of Slags on Phytoplankton

Results of Exp 1 which was done in the medium prepared from natural seawater indicate that there exists an optimal concentration of slags enriched as a nutrient source for phytoplankton. When the de-C and de-P slags supplied at 330 mg/l and more, growth of phytoplankton was inhibited. Although concentrations of released P and Si were highest when de-C slag was added at 330 mg/l, final yield was suppressed to 64% of that in control (Fig. 4A). The highest addition at 3 300 mg/l inhibited growth completely. This suppression may be responsible for the excessive P increase (Fig. 2). Changes of pH in seawater influence the inter-speciation of inorganic carbon. As pH increases, equilibrium between CO$_2$, aq., HCO$_3^-$, CO$_3^{2-}$ shifts toward HCO$_3^-$ and CO$_3^{2-}$, which are less available form for marine phytoplankton. None of the species attained their maximum growth rate above pH 9 and many species could not growed at pH close to 10.\(^{21}\) On the other hand, enrichment of de-C slag at less than 3.3 mg/l did not affect growth of phytoplankton, while at 33 mg/l the growth was slightly enhanced (Fig. 4). This enhancement would be attributed to P released from the slag, because P exhausted at the end of incubation at 3.3 mg/l or lower treatments (Table 3). However, the enhancement was much lower than expected from the amount of P and Si released from de-C slag. This was at-
tributed to lack of nitrogen. N:P ratio of original seawater was 13:1, which is lower than phytoplankton requirement, and then nitrogen was actually exhausted at the end of incubation (Table 3). Although concentration of P and Si never increased in de-P slag treatment, growth was enhanced as seen in de-C slag treatment. This indicates that release of P from the de-P slag was promoted by a certain biological activities in the culture experiments. The activities such as photosynthesis and respiration alter pH of the medium diurnally and particularly the respiration at night decreases pH which in turn accelerates dissolution of PO$_4^{3-}$.

In Exp 2 medium was prepared with plenty nitrogen to avoid nitrogen limitation during culture experiments. Then Thalassiosira guillardii increased with addition of de-C slag at $\geq$3.3 mg/l in ex P media where reagent P was not added (Figs. 5(B), 5(F)). This evidently shows that $T. guillardii$ can grow on released P from the slag. However, $T. guillardii$ was not able to grow in ex Fe/P and ex Fe media, where reagent Fe was not added (Figs. 5(E), 5(G)). When the Enrichment solution Fe (6.6 $\mu$M) was added to these cultures on Day 8, $T. guillardii$ started to grow (Fig. 7). This result indicates that dissolution of Fe from the slag did not take place in the artificial seawater without EDTA. In oxic seawater concentration of dissolved inorganic Fe which presents mainly as Fe(III) is very low because it is very unstable and easily precipitates as oxyhydroxides. Organic ligands help to stay Fe(III) unoxidated in natural seawater and more than 99.9% of dissolved Fe(III) is estimated to be chelated with the ligands. In the present experiments, however, EDTA was effective to keep available Fe for phytoplankton growth under a limited condition, while Fe was not always available when a slag solution extracted without EDTA. Especially when concentrations of PO$_4^{3-}$ and slag were high, availability of the Fe originating from the slag was low even when the slag solution was made with EDTA (Fig. 6). This indicates that Fe retained by EDTA and dissolved inorganic Fe in solution as well can be precipitated with PO$_4^{3-}$ under high pH and solubility of Fe decreases. CaO in slag increases pH of water and then alkaline condition prevents dissolution of Fe. Contrary to the effect, Ca$^{2+}$ scavenges PO$_4^{3-}$ and helps Fe from precipitate with PO$_4^{3-}$ so that slag addition into medium makes solubility of Fe complex. Therefore, small amount of the slags can be applied (Fig. 2). Even if only a small amount of Fe can be released from such a small amount of the slags, phytoplankton can grow actively because of their low Fe requirement (C:N:P:Fe=106:16:1:0.0035). If the slag particles instead of slag solution had been added directly to the culture, Fe might have been released as P was released under biological activities in Exp 1. In fact, addition of de-C slag of 5.5 mg/l enhanced growth of phytoplankton assemblage in the HNLC region of the North Pacific where phytoplankton growth was limited by Fe.

Among nutrients controlling productivity of phytoplankton assemblages, Si is required by a particular kind of phytoplankters such as diatoms and silicoflagellates. Therefore, availability of Si is a major factor controlling the taxonomic structure of the assemblages. Major input of Si to ocean in nature is river runoff and most human activities tend to decrease the Si delivery to ocean, while other nutrients are usually input superfluously to coastal waters. Si released from the slags would then recover an unbalanced nutrient composition in the coastal waters.

5. Conclusion

Our results evidently show that the steelmaking slags have positive effects on the growth of marine phytoplankton. In Exp 1 a coastal seawater including a natural phytoplankton assemblage was incubated with decarburization (de-C) and dephosphorous (de-P) slag particle at different concentrations under freely drifting pH. Result of the Exp 1 indicates that there exists an optimal concentration of slags enriched as a nutrient source. When de-C and de-P slags supplied at 330 mg/l and more, growth of phytoplankton was inhibited by excessive pH increase. On the other hand, growth of natural phytoplankton assemblage was enhanced by addition of the slags at 33 mg/l, where pH slightly increased to 8.3 (Fig. 4). However, the enhancement was much lower than expected from the amount of P and Si released from slags. This was attributed to lack of nitrogen in original seawater.

In Exp 2, medium was prepared with plenty nitrogen to avoid nitrogen limitation during culture experiments and inoculated with a pure culture of the centric diatom Thalassiosira guillardii to eliminate effects of grazers on phytoplankton. This result evidently shows that $T. guillardii$ can grow on released P from the de-C slag (Figs. 5(B), 5(F)). However, $T. guillardii$ was not able to grow in ex Fe/P and ex Fe media, where reagent Fe was not added (Fig. 5(E), 5(G)). It is conceivable that increased pH to 9.3 decrease solubility of Fe in the process of making slag solution. If the slag particles instead of slag solution had been added directly to the culture, Fe might have been released. In fact, addition of de-C slag at 5.5 mg/l enhanced growth of phytoplankton assemblage in the HNLC region of the North Pacific.
Pacific where phytoplankton growth was limited by Fe.\(^{26}\)

These results suggest that slags can be effective sources of PO\(_4^{3-}\) and Si for phytoplankton growth and can mitigate extremely hyper-nitrogenous environments caused by discharge of municipal sewage. Slag enrichment would also be an effective way of recycling massive amount of nitrogen. Phytoplankton (organic products) will be a food for filter feeding zooplankton and contribute to build the large fishable populations. However, excess enrichment of the slags (e.g. over 3 300 mg/l) not only suppresses release of PO\(_4^{3-}\), Si and Fe but also inhibits growth of phytoplankton. A low dose of the slag avoiding pH increase is recommended in case of enrichment in field. Since the effective dose may be variable with kind of slags, it should be determined for each slag to be used.

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